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(54) 【発明の名称】 リチウム二次電池負極用材料およびその製造方法並びにリチウム二次電池

(57) 【要約】

【課題】 天然黒鉛等の鱗片状黒鉛の最高水準の放電容量もしくは黒鉛構造から決定される理論容量と同程度の放電容量を持つと共に、かつ充電初期における副反応に起因する不可逆容量が大きく、大きな充放電電流下で使用了場合に高い放電容量が得られない等の鱗片状黒鉛の問題を解決したリチウム二次電池用負極材料、およびその製造方法、並びにこれを用いたリチウム二次電池を工業的に提供する。

【解決手段】 金属と炭素の熔融状態の冷却過程に析出した炭素を処理して得られる炭素含有量が90質量%以上の黒鉛と炭素質バインダーとの捏合物を熱処理してなる炭素材料であり、所定の平均粒径範囲及びタップ密度範囲を満足するリチウム二次電池負極用材料とその製造方法、及びこれを負極活物質として用いてなるリチウム二次電池を提供する。

【特許請求の範囲】

【請求項1】 金属と炭素の熔融状態の冷却過程に析出した炭素を処理して得られる炭素含有量が90質量%以上の黒鉛と、炭素質バインダーとの捏合物を、熱処理してなる炭素材料であって、該炭素材料の平均粒径が5 μ m以上100 μ m未満、かつ20回タップ時のタップ密度が0.70 g/cm³以上であることを特徴とするリチウム二次電池負極用材料。

【請求項2】 前記捏合物の炭素質バインダーが、熱処理により炭素化物になっていることを特徴とする請求項1記載のリチウム二次電池負極用材料。

【請求項3】 前記炭素材料が、黒鉛化物であることを特徴とする請求項1記載のリチウム二次電池負極用材料。

【請求項4】 前記炭素材料の300回タップ時のタップ密度が0.85 g/cm³以上であることを特徴とする請求項1～3の何れか1項に記載のリチウム二次電池負極用材料。

【請求項5】 前記炭素材料の炭素含有量が99質量%以上で、BET法による比表面積が5 m²/g以下であることを特徴とする請求項1～4の何れか1項に記載のリチウム二次電池負極用材料。

【請求項6】 金属と炭素の熔融状態の冷却過程に析出した炭素を、炭素含有量が90質量%以上になるまで高純度化処理を行った後に、インペラーミル、ジェットミル、レイモンドミルまたはボールミルより選ばれた粉砕機を用いた粉砕と空気分級を行うことにより得られた黒鉛と、炭素質バインダーとを捏合し、該捏合物を700～1500℃で炭化及び/または2400～3000℃で黒鉛化することを特徴とするリチウム二次電池負極用材料の製造方法。

【請求項7】 前記金属は、鉄、ニッケル、シリコンおよびコバルトからなる群より選択される1種または2種以上の金属であることを特徴とする請求項6記載のリチウム二次電池負極用材料の製造方法。

【請求項8】 金属と炭素の熔融状態が、製鉄プロセスの熔融鉄における鉄と炭素の熔融状態であることを特徴とする請求項6記載のリチウム二次電池負極用材料の製造方法。

【請求項9】 前記黒鉛の平均粒径が3 μ m以上30 μ m以下であることを特徴とする請求項6～8の何れか1項に記載のリチウム二次電池負極用材料の製造方法。

【請求項10】 前記黒鉛と前記炭素質バインダーを、該炭素質バインダーの軟化点以上の温度に加熱しながら攪拌、捏合することを特徴とする請求項6～9の何れか1項に記載のリチウム二次電池負極用材料の製造方法。

【請求項11】 前記黒鉛と前記炭素質バインダーの捏合割合が、黒鉛100質量部に対して、炭素質バインダーが10～70質量部であることを特徴とする請求項6～10の何れか1項に記載のリチウム二次電池負極用材

料の製造方法。

【請求項12】 正極活物質と、請求項1～5の何れか1項に記載のリチウム二次電池負極用材料を含んでなる負極活物質と、非水系電解質とを含んでなるリチウム二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、リチウムの挿入、脱離反応を利用するリチウム二次電池およびこれに用いられる負極活物質に関するものである。さらに詳しくは、放電容量が大きく、且つ、充放電時の容量ロスのない高性能なリチウム二次電池およびこれに用いられる負極活物質に関するものである。

【0002】

【従来の技術】黒鉛等の炭素材料を負極として用いるリチウム二次電池は、金属リチウムを用いた場合に問題となる充電時のデンドライト生成がなく、信頼性の高い電池であることから活発に研究されている。特に、炭素材料として黒鉛を用いた場合は、充電時にリチウムが黒鉛層間に挿入した、いわゆる黒鉛層間化合物を形成することにより、充電時にリチウムが負極中に吸蔵され、負極材料に金属リチウムを用いた際に問題となるデンドライトの生成が抑止され、かつ放電電位も金属リチウムを用いた場合に比べ、0～0.1V程度高いに過ぎないために、高起電力が得られるといった優れた特性を持つ。

【0003】ただし、黒鉛材料と分類される炭素は、その形状、構造、組織は多様であり、この違いが電極性能に反映される。

【0004】黒鉛材料として天然黒鉛等の鱗片状黒鉛を用いた場合、その高度に発達した黒鉛結晶構造により、以下で述べるメソフェーズ小球体、ピッチ系炭素繊維、ピッチコークス等を黒鉛化焼成して得られる人造黒鉛に比べて、高い放電容量が得られることが知られている

(例えば、第40回電池討論会1D14)。しかしながら、これら鱗片状黒鉛においては、初期充電過程において、主として黒鉛層構造端部近傍で進行する副反応に起因する初期不可逆容量が大きいという問題がある。加えて、天然黒鉛においては、これらの結晶構造は、炭素網面層が特定方向への優先配向をしているため、材料中のリチウムの拡散方向が限定され、しかも、その拡散距離が非常に長い。従って、大きな充放電電流下で使用した場合、高い放電容量を得ることは難しく、実用上の制約を受けるものと思われる。

【0005】黒鉛材料として、メソフェーズピッチの光学的異方性相が球状に生成した段階で採取して調製したメソフェーズ小球体を用いた場合、黒鉛化後の炭素層面の発達が天然黒鉛に比べて劣ることにより、理論的放電容量に比べて80～85%程度の放電容量しか得られないという問題がある。

【0006】ピッチ系炭素繊維も、超高温の温度領域で

の黒鉛化処理により人造黒鉛としての種々特性を備え、かつリチウムの拡散方向が繊維外周から内部へ向かっての多方向、かつ拡散距離が繊維外周から繊維軸までの繊維径の半分の数 μm 程度と短いため、この炭素繊維を粉碎した粉末は、拡散係数が他の易黒鉛化性材料と比較して大きく、重負荷特性を確認したとの報告(J. Electrochem. Soc., 142, 8, 2564 (1995))もされている。しかし、繊維の形態を維持するがゆえに、熱処理温度を高くしても、結晶構造の発達が阻害されて、放電容量が大きくなること、繊維の形態を確保するためのピッチの高純度化処理、繊維化工程等が必要なため、黒鉛化処理前の段階で他材料と比較してより多くの製造コストがかかるなどの問題がある。

【0007】ピッチコークスは、易黒鉛化性材料の部類に属し、超高温の温度領域での黒鉛化処理により、天然黒鉛に近い炭素網面層の層間距離に近づくが、コークスの持つ光学的異方性組織により、天然黒鉛ほど黒鉛化が発達せず、これらの結晶構造は、炭素網面層が特定方向への優先配向をしていない。従って、天然黒鉛等の鱗片状黒鉛に見られた電流密度下の制約は無く、リチウム二次電池用負極材料として非常に有望な材料であり、これまで多くの研究がなされている(例えば、特開昭63-121257号公報、特開平1-204361号公報、特開平4-206276号公報など)。しかしながら、通常のピッチコークスの超高温処理(2000~3000℃焼成)品の放電容量は、理論容量(372mAh/g)と比較して低い(<300mAh/g)という問題が有る。

【0008】以上のように、リチウム二次電池の負極活物質として種々の黒鉛材料を用いる際に、高い放電容量を得るためには、高度に発達した黒鉛層状構造が必要である。この目的で、天然黒鉛等の鱗片状黒鉛を使用した場合には、初期不可逆容量が大きく、大きな充放電電流下で良好な特性が得られない等の問題があった。一方、メソフェーズ小球体、ピッチ系炭素繊維あるいはピッチコークスを用いた場合には、その黒鉛構造の発達程度が鱗片状黒鉛に及ばないため、高い放電容量が得られないという実用上の問題があった。

【0009】

【発明が解決しようとする課題】本発明は、リチウム二次電池負極用炭素材料として、天然黒鉛等の鱗片状黒鉛の最高水準の放電容量もしくは黒鉛構造から決定される理論容量と同程度の放電容量を持つと共に、かつ充電初期における副反応に起因する不可逆容量が大きく、大きな充放電電流下で使用した場合に高い放電容量が得られない等の鱗片状黒鉛の問題を解決した、リチウム二次電池用負極材料およびその製造方法並びにこれを用いたリチウム二次電池を工業的に提供することを目的とする。

【0010】

【課題を解決するための手段】本発明者らは、各種黒鉛材料の粒子形状、生成過程、構造及び粒度等の粉体特性と電気的物性との関連を鋭意検討した結果、金属と炭素の熔融状態の冷却過程に析出した炭素を用いて、これを炭素質バインダーと捏合して捏合物とした後、炭化及び/または黒鉛化を行うことにより、これをリチウム二次電池の負極として用いることができ、かつこのリチウム二次電池負極用材料が高い放電容量を示すと共に、従来放電容量の大きな鱗片状黒鉛で問題となっていた不可逆容量が大きい等の問題を大きく改善できる材料であることを見出した。かかる知見に基づいて、リチウム二次電池の負極としての電極特性に優れるリチウム二次電池負極用炭素材料およびその製造方法並びにこれを用いたリチウム二次電池を提供するに至った。

- 15 【0011】即ち、本発明は、(1) 金属と炭素の熔融状態の冷却過程に析出した炭素を処理して得られる炭素含有量が90質量%以上の黒鉛と、炭素質バインダーとの捏合物を、熱処理してなる炭素材料であって、該炭素材料の平均粒径が5 μm 以上100 μm 未満、かつ200回タップ時のタップ密度が0.70g/cm³以上であることを特徴とするリチウム二次電池負極用材料、
- 20 (2) 前記捏合物の炭素質バインダーが熱処理により炭素化物になっていることを特徴とする(1)記載のリチウム二次電池負極用材料、(3) 前記炭素材料が、黒鉛化物であることを特徴とする(1)記載のリチウム二次電池負極用材料、(4) 前記炭素材料の300回
- 25 タップ時のタップ密度が0.85g/cm³以上であることを特徴とする(1)~(3)の何れか1項に記載のリチウム二次電池負極用材料、(5) 前記炭素材料の炭素含有量が99質量%以上で、BET法による比表面積が5m²/g以下であることを特徴とする(1)~
- 30 (4)の何れか1項に記載のリチウム二次電池負極用材料、(6) 金属と炭素の熔融状態の冷却過程に析出した炭素を、炭素含有量が90質量%以上になるまで高純度化処理を行った後に、インペラーミル、ジェットミル、レイモンドミルまたはボールミルより選ばれた粉碎機を用いた粉碎と空気分級を行うことにより得られた黒鉛と、炭素質バインダーとを捏合し、該捏合物を700~1500℃で炭化及び/または2400~3000℃
- 35 で黒鉛化することを特徴とするリチウム二次電池用負極用材料の製造方法、(7) 前記金属は、鉄、ニッケル、シリコンおよびコバルトからなる群より選択される1種または2種以上の金属であることを特徴とする
- 40 (6)記載のリチウム二次電池負極用材料の製造方法、(8) 金属と炭素の熔融状態が、製鉄プロセスの溶銑鉄における鉄と炭素の熔融状態であることを特徴とする(6)記載のリチウム二次電池負極用材料の製造方法、(9) 前記黒鉛の平均粒径が3 μm 以上30 μm 以下であることを特徴とする(6)~(8)のいずれか
- 45 1項に記載のリチウム二次電池負極用材料の製造方法、

(10) 前記黒鉛と前記炭素質バインダーを、該炭素質バインダーの軟化点以上の温度に加熱しながら攪拌、捏合することを特徴とする(6)～(9)の何れか1項に記載のリチウム二次電池負極用材料の製造方法、(11) 前記黒鉛と前記炭素質バインダーの捏合割合が、黒鉛100質量部に対して、炭素質バインダーが10～70質量部であることを特徴とする(6)～(10)の何れか1項に記載のリチウム二次電池負極用材料の製造方法、(12) 正極活物質と、請求項1～5の何れか1項に記載のリチウム二次電池負極用材料を含んでなる負極活物質と、非水系電解質とを含んでなるリチウム二次電池である。

【0012】

【発明の実施の形態】以下に、本発明の内容について具体的に説明する。

【0013】本発明に係るリチウム二次電池負極用黒鉛は、金属と炭素の熔融状態の冷却過程で析出した炭素を処理して得られる炭素含有量が90質量%以上の黒鉛と炭素質バインダーを捏合して捏合物とした後熱処理を行い、これを平均粒径が $5\mu\text{m}$ 以上 $100\mu\text{m}$ 未満、かつ20回タップ時のタップ密度が $0.70\text{g}/\text{cm}^3$ 以上に調製することにより得られるリチウム二次電池負極用材料である。

【0014】本発明のリチウム二次電池負極用黒鉛の要件としては、第一に、原料として用いる黒鉛を、人造黒鉛でありながら天然黒鉛に匹敵する高度な黒鉛構造を得るために、金属との熔融状態から析出せしめること、第二に、この黒鉛の炭素含有量を最適な範囲に制御すること、第三に、この黒鉛と炭素質バインダーを捏合して捏合物とした後に熱処理を行うこと、第四に、これを平均粒径 $5\mu\text{m}$ 以上 $100\mu\text{m}$ 未満、かつ20回タップ時のタップ密度 $0.70\text{g}/\text{cm}^3$ 以上となる様に調製することにある。以上の第一から第四まですべての要件を合わせて、以下の記述にて上記要件(1)と呼ぶ。

【0015】第一の要件である、原料として用いる黒鉛を、人造黒鉛でありながら天然黒鉛に匹敵する高度な黒鉛構造を得るために、金属との熔融状態から析出せしめることに関して説明する。

【0016】本発明のリチウム二次電池負極用材料の原料として用いる黒鉛は、その生成過程における天然黒鉛と人造黒鉛という区分において、人造黒鉛に属する。人造黒鉛を製造する方法としては、炭素を主成分とする原料を用いて、最終的に 2000°C から 3000°C の高温で熱処理することが最も一般的である。しかし、この方法を用いた場合に得られる人造黒鉛では、天然黒鉛に比較して、黒鉛構造が十分に進行しないため、黒鉛化度は劣る。一方、金属と炭素の熔融状態の冷却過程で析出した炭素は、高度に発達した黒鉛構造をとる。これは、炭素が熔融相から析出する際、熱力学的に安定な黒鉛を形成することによる。この高度に発達した黒鉛構造と天然

黒鉛等鱗片状黒鉛における本質的差異の詳細は未だ明らかではないが、本発明のリチウム二次電池負極用黒鉛の電気的性能において、天然黒鉛等の鱗片状黒鉛で問題となっていた不可逆容量が大きい等の問題を大きく改善できる。これは、天然黒鉛は、黒鉛粒子がほぼ単結晶黒鉛から成り、かつその結晶配向がほぼ一方向になっているのに対し、本発明の原料である黒鉛粒子は、黒鉛多結晶から成っており、しかもその配向が天然黒鉛に比較して、多方向になっていることに起因すると推定される。

【0017】また、第二の要件である原料として用いる炭素含有量に関して説明する。

【0018】リチウム二次電池用負極材料として、黒鉛を用いることの大きな意義の一つは、充放電過程の化学変化、即ち、充電時に黒鉛層間に Li^+ イオンが挿入されて、黒鉛層間化合物を形成し、放電時にリチウムイオンが脱離して、黒鉛に戻る反応における電位が、リチウム金属とリチウムイオンの変化における電位と同等であり、かつ、使用領域の大部分で平坦な放電曲線が得られることである。本発明で得られるリチウム二次電池負極材料の充放電容量の大部分は、原料として用いる黒鉛により得られるものである。即ち、炭素質バインダーと捏合した後に炭化及び/または黒鉛化を経ることにより、バインダー成分が炭化または黒鉛化されて、放電容量に寄与するものの、本発明で得られるリチウム二次電池負極材料が特徴とする高い放電容量が得られるのは、原料の黒鉛自体の高い放電容量に起因するものである。従って、原料となる黒鉛の純度が低い場合には、それより得られる負極材料中の充放電反応に関与する黒鉛の割合が小さくなり、負極材料として高い放電容量を担うことはできない。仮に、負極材料中の黒鉛が、その理論放電容量である $372\text{mAh}/\text{g}$ の放電容量を持っていたとしても、その含有量が少なくとも90質量%以上無ければ、その放電容量は $335\text{mAh}/\text{g}$ に達しないため、高放電容量の負極材料は得られないし、天然黒鉛等の鱗片状黒鉛以外では通常達成されない $350\text{mAh}/\text{g}$ 以上の高い放電容量が得るという点からは、更に望ましい黒鉛の炭素含有量は95質量%以上である。以上から、本発明のリチウム二次電池負極用材料の原料として用いる黒鉛の炭素含有量が90質量%以上、望ましくは95質量%以上と規定される。炭素濃度90質量%以上の範囲を満足する黒鉛は、工業的に良く知られた浮遊選鉱法、酸処理、高温熱処理等の精製プロセスを、単独あるいは組み合わせて用いることにより容易に得られる。

【0019】また、第三の要件である、原料である黒鉛と炭素質バインダーを捏合して捏合物とした後に、熱処理を行うことに関して説明する。そもそも本処理の最大の意義は、原料として用いる黒鉛が有する理論容量に匹敵する高い放電容量を維持しつつ、捏合による粒子の適正な造粒または接着によって、不可逆容量の低減や比表面積、タップ密度等の粉体性状の向上を図ることにあ

る。炭素質バインダーとしては、コールタールピッチ、石油ピッチ、ナフタレンピッチ等のピッチ、3, 5-ジメチルフェノールホルムアルデヒド樹脂、ポリ塩化ビニル等の炭素を主成分としたものがあげられ、これらを溶融したものや平均粒径 $5 \sim 300 \mu\text{m}$ に粉碎したものが用いられる。また、この捏合とは、黒鉛粉末と炭素質バインダーを原料にして、緻密な黒鉛製品を製造するような、従来炭素材料分野で広く用いられていた方法の応用である。その一例を示すと、先ず、両者を混合した後、加熱しながら攪拌、捏合する。これにより、上記黒鉛と炭素質バインダーとの捏合物、すなわち、ビーズ状の造粒物が得られる。この造粒物を熱処理することにより、炭素質バインダー中の有機物が炭化または黒鉛化されリチウムイオンの吸脱着あるいは挿入脱離に関与することができる。この熱処理を行わない場合、炭素質バインダーは、熱的、化学的に安定化していないと共に、リチウムイオンの吸脱着性能が極めて劣っている。加えて、熱処理した炭素質バインダーは、前記黒鉛粉末の造粒、接着の役割によって、副反応の低減や粉体性状の改善を可能とするものであり、この意味でも適正な熱処理が不可欠である。

【0020】また、第四の要件である、前記の捏合物を平均粒径 $5 \mu\text{m}$ 以上 $100 \mu\text{m}$ 未満、かつ20回タップ時のタップ密度を 0.70 g/cm^3 以上となるように調製することに関して説明する。平均粒径が $5 \mu\text{m}$ 未満と小さい場合は、比表面積の増加による不可逆容量の増加や高密度の低下、負極電極作製における塗工面に不均一が発生する等の問題を生じ、また、平均粒径が $100 \mu\text{m}$ を超えて大きい場合、リチウム二次電池負極として電極箔に塗布した際に、必要な平滑性が得られない等の問題が生じる。更に、充放電時での反応の均一性、粒子内部での Li イオンの拡散のしやすさから平均粒径 $50 \mu\text{m}$ 以下であることがより望ましい。この平均粒度範囲を満足し、かつ20回タップ時のタップ密度が 0.70 g/cm^3 以上となるように、捏合物の粉碎、粒度調整を行うことにより優れたリチウム二次電池用負極材料が得られる。このタップ密度を最適な範囲に制御することに関して説明する。黒鉛粉末材料のタップ密度の測定法は JIS-K5101 に規定されており、これに準拠して測定した。このタップ密度を20回のタップ回数で規定することについては、粉体のタップ密度はそのタップ回数に従って上昇するが、電極製造時の安定性や操作性は、タップ回数の少ない場合のタップ密度に強く依存する。また、20回未満のタップ時のタップ密度の規定でも同様の定義が可能だが、測定精度や測定値の再現性の点から、タップ回数20回の規定が最適であると考え、ここに規定した。リチウム二次電池負極用材料としての黒鉛において、タップ密度を向上させることは、電極箔塗工工程の安定操業を容易にするのみならず、材料の運送、保管等の操作においても重要である。例えば、類似

の粒度分布を持つ天然黒鉛と、メソフェーズ小球体を比較すると、天然黒鉛のタップ密度は $1/3 \sim 1/5$ と低く、これがために塗工液作製時に同質量の黒鉛を用いた場合に、その液粘度は極めて大きくなり、均一な塗工がより困難になる等の問題を生じる。この平均粒径とタップ密度の制御を行うことは、捏合物の原料として用いる黒鉛の平均粒径及び粒度分布を適性に制御すること、及び/または、得られた捏合物を、冷却後に、所定の粒度になるまで粉碎及び必要に応じて分級することにより達成される。原料黒鉛の平均粒度は、目的とする最終生成物の平均粒度以下とすることが好ましいし、捏合物を粉碎、分級した際の粒径は、出発原料となる黒鉛の粒径より大きくするのが好ましい。生成物であるリチウム二次電池負極用材料の平均粒径を出発原料の粒径より小さくすると、出発原料である黒鉛粒子の破壊が起こり、性能上望ましくない。即ち、本発明のリチウム二次電池負極用材料において、平均粒径 $5 \mu\text{m}$ 以上 $100 \mu\text{m}$ 未満、かつ20回タップ時のタップ密度が 0.70 g/cm^3 以上を満足すれば、天然黒鉛で見られた塗工液作製の際の困難を回避できることがわかった。

【0021】以上のように、上記要件(1)、即ち前記第一から第四までのすべての要件を同時に満たすことにより、リチウム二次電池負極用炭素材料として、天然黒鉛等の鱗片状黒鉛の最高水準の放電容量もしくは黒鉛構造から決定される理論容量と同程度の放電容量を持つと共に、かつ充電初期における副反応に起因する不可逆容量が小さく、大きな充放電電流下で使用した場合に高い放電容量が得られる等の優れた特性が得られ、鱗片状黒鉛の問題を解決したリチウム二次電池負極用材料が提供されるに至った。

【0022】更に、本発明のリチウム二次電池負極用材料の要件として、上記要件(1)に加えて、前記捏合物の炭素質バインダーが熱処理により炭化物になっても良い。これを以下の記述にて上記要件(2)と呼ぶ。

【0023】前記捏合物を熱処理して捏合物を炭化するためには、非酸化性雰囲気下で 700°C 以上 1500°C 以下の温度で熱処理することが望ましい。 700°C 以上 1500°C 以下での熱処理は、捏合物中の炭素質バインダーに含まれる揮発成分を飛散させ、かつ炭素質バインダーを炭化させるものである。その温度は、炭素質バインダーの種類に併せて、上記温度範囲内で適切な温度を設定すれば良い。この加熱温度が 700°C より低いと、炭素質バインダーを十分に炭化しにくい。また、 1500°C より高くても良いが、 1500°C 程度あれば、バインダーの揮発成分はほぼ飛散し、炭化の目的をほぼ達成することができるので、 1500°C 程度で充分である。即ち、上記要件(1)に加えて、熱処理によって捏合物の炭素質バインダーを炭化物とした本発明の材料は、リチウム二次電池負極用炭素材料として優れた特性を示す。

【0024】また、本発明のリチウム二次電池負極用材料の要件として、上記要件（１）に加えて、前記炭素材料が、黒鉛化合物であることが好ましい。これを以下の記述にて上記要件（３）と呼ぶ。この黒鉛化合物は、前記捏合物を必要に応じて炭化処理を行った後、 2400°C 以上 3000°C 以下で黒鉛化することにより得られる。黒鉛化に先立つ炭化処理は、通常、 700°C 以上 1500°C 以下程度の温度で行い、黒鉛化処理での操業安定性、安全性の点で行うことが望ましいが、これらの問題が回避可能であれば、目的の材料を得るために炭化処理は省略可能である。即ち、黒鉛化処理によって、本発明の効果が更に顕著に得られる。即ち、この温度領域での熱処理により、黒鉛の純化と炭素質バインダーの黒鉛化が同時に進行し、これらにより放電容量の更なる増加が得られる。この黒鉛化温度が 2400°C 未満では、炭素質バインダーの黒鉛化が充分に進まず、処理の効果である放電容量の増加は充分に得られない。また、 3000°C より高くても良いが、安全性や経済性から 3000°C 以下で充分である。即ち、上記要件（１）に加えて、前記炭素材料を黒鉛化合物とすることにより得られる材料は、リチウム二次電池負極用材料として優れた特性を示す。

【0025】さらに、本発明のリチウム二次電池負極用材料の要件として、上記要件（１）～（３）に加えて、 300 回タップ時のタップ密度が 0.85 g/cm^3 以上であることが好ましい。これを以下の記述にて上記要件（４）と呼ぶ。即ち、上記要件（４）は、上記要件（１）で規定した 20 回タップ時のタップ密度が 0.70 g/cm^3 以上という要件に加えて、 300 回タップ時のタップ密度 0.85 g/cm^3 を満足することにより、粉体としての特性がさらに改善されるというものである。本発明の上記要件（１）の規定の説明において、電極製造時の安定性や操作性はタップ回数の少ない場合のタップ密度（本発明で 20 回タップ時を規定）に強く依存することを述べたが、ここで更に、 300 回タップ時のタップ密度を規定することにより、平均粒度が一定範囲、かつタップ回数が少ない場合の適正なタップ密度を満足した上で、タップ回数が多い場合のタップ密度を一定以上に成さしめることで、更に顕著に本発明の効果を発揮することを見出したものである。例えば、 20 回タップ時のタップ密度が 0.70 g/cm^3 以上で同等である２種類の粉体Ａ、Ｂにおいて、粉体Ａの 300 回タップ時のタップ密度が 0.85 g/cm^3 未満、粉体Ｂのそれが 0.85 g/cm^3 以上であるとすると、電極箔塗工工程での溶媒を用いたスラリー作製時や、塗工後の電極箔プレスの際の操作性において、粉体Ｂの方が操作性が容易かつ製造した電極箔の安定性は優れている。これは、スラリー作製時の混練工程や塗工後のプレス工程においては、一定以上の嵩密度を出発状態として、さらに高い嵩密度への変化が起こることから、その変化の容易さが 300 回タップ時のタップ密度で表現されるもの

と考えられる。即ち、 300 回タップ密度が 0.85 g/cm^3 以上であれば、本発明の効果がさらに顕著に示されることが分かった。

【0026】さらに、本発明のリチウム二次電池負極用材料の要件として、上記要件（１）～（４）に加えて、炭素含有量が 99 質量％以上、かつＢＥＴ法による比表面積が $5\text{ m}^2/\text{g}$ 以下であるものが好ましい。即ち、上記要件（１）～（４）に加えて、炭素含有量を一定の割合以上に高めること、比表面積を一定の値以下に制御することのすべてを満たすものである。これを以下の記述にて、上記要件（５）と呼ぶ。本要件を構成する因子である、リチウム二次電池負極用材料の炭素含有量に関して説明する。この炭素含有量が高いほど、リチウムイオンの挿入、脱離に關与する黒鉛構造の割合が大きいため、負極材料として得られる放電容量が大きくなるが、これに加えて、鉄等の金属元素や吸着水分等、炭素以外の元素、化合物の含有量を少なくすることが重要である。炭素含有量が 99 質量％未満の場合、不純物金属の影響により、電解液等の劣化によるサイクル特性の低下や不可逆容量の増加が、また、水分の影響により、非水電解液の劣化や塗工工程での塗工液の安定性低下等の問題が生じる。これらの悪影響を低減するために、炭素含有量を 99 質量％以上、好ましくは 99.5 質量％以上とする。

【0027】また、同じくＢＥＴ比表面積に関して説明する。ＢＥＴ比表面積は、黒鉛粉末の比表面積を記述する一般的な指標として、当業界を始め炭素、黒鉛に関連する技術分野で広く用いられている。これは、予め吸着物を脱離させて、真空容器に入れた粉末に、液体窒素温度にて窒素ガスを吸着させて、その等温吸着曲線を求めることにより得られる。このＢＥＴ法による比表面積が $5\text{ m}^2/\text{g}$ 超とした場合、負極電極作製の際に塗工面にむらや不均一部分が発生する、あるいは大気中水分の吸着が顕著となり不純物濃度が増加する、あるいは充放電初期の副反応が増大する等、電極性能の劣化が顕著となる。

【0028】以上の要件を満たすことにより、リチウム二次電池負極用炭素材料として、天然黒鉛等の鱗片状黒鉛の最高水準の放電容量もしくは黒鉛構造から決定される理論容量と同程度の放電容量を持つと共に、かつ充電初期における副反応に起因する不可逆容量が小さく、大きな充放電電流下で使用した場合に高い放電容量が得られる等の優れた特性が得られ、鱗片状黒鉛の問題を解決したリチウム二次電池用負極材料が提供されることを示された。

【0029】次に、上記本発明のリチウム二次電池負極用黒鉛の製造方法について説明する。

【0030】本発明の製造方法は、金属と炭素の溶融状態の冷却過程に析出した炭素の処理が、炭素含有量が 90 質量％以上に達するまで高純度化処理を行った後に、

インペラーミル、ジェットミル、レイモンドミルまたはボールミルより選ばれた粉碎機を用いた粉碎と空気分級を行い、得られた黒鉛を、炭素質バインダーと捏合し、該捏合物を 700～1500℃で炭化及び／または 2400～3000℃で黒鉛化することを特徴とする、リチウム二次電池負極用材料の製造方法である。本要件を以下の記述で、上記要件（6）と呼ぶ。即ち、上記要件（6）は、優れたリチウム二次電池負極用材料を容易にかつ工業的に製造する目的で、先ず原料黒鉛を得る際に、金属と炭素の熔融状態の冷却過程に析出した炭素の高純度化処理を行い、一定以上の炭素含有量とした後に、最適な粉碎機を用いた粉碎と空気分級で粒度調整を行い、これを原料としてバインダーとの捏合物を得た後、最適な熱処理をすることを特徴とする製造方法である。本発明の製造方法により、優れた特性を持つリチウム二次電池負極用材料を、より容易にかつ高い工程歩留で得ることが可能である。ここで言う高純度化とは、金属と炭素の熔融状態の冷却過程に析出した炭素の炭素含有量を 90 質量％以上に高めるための処理であり、浮遊選鉱法、酸処理、高温熱処理等の一般に知られた精製プロセスを単独あるいは組み合わせて用いることである。高純度化処理を行う前に粉碎、分級といった粒度調整を行った場合は、高純度化処理で大部分の金属粒子が脱離すること等に起因する粒度変化により、原料である黒鉛の平均粒度を制御することが困難である。また、高純度化の後に粉碎を行わなければ、所定の平均粒度を持つ製品を高い歩留で得ることはできない。また、インペラーミル、ジェットミル、レイモンドミル、ボールミルより選ばれる粉碎機を用いることにより、粉碎を経ていない黒鉛を用いる場合に比べて、生成したリチウム二次電池負極用材料の高密度、タップ密度等の粉体特性値の向上が容易になし得る。これは、原料を粉碎する効果として、高純度化処理直後に存在する鱗片状粒子の形状が、粉碎工程中に角がとれて、より球状に近く変化し、これが炭素質バインダーとの捏合やその後の炭化、黒鉛化といった処理を経て製造されるリチウム二次電池負極用材料の物性にも反映されることによる。この粉碎工程において、鱗片状粒子の大部分の形状を変化させ、曲面形状粒子にならしめることが、上記要件（6）の根幹をなすものである。粉碎現象そのものは、粒子が割れたり、欠けたりするものであるが、粉碎機内部において、粒子同士が接触、衝突、摩耗を繰り返すことにより、鱗片状黒鉛粒子が曲面形状粒子に変化して、リチウム二次電池負極用材料の原料黒鉛としての高い適性が得られると推定される。この黒鉛を炭素質バインダーと捏合して、捏合物を得た後、該捏合物を 700℃以上 1500℃以下で炭化及び／または 2400℃以上 3000℃以下で黒鉛化することにより、目的とするリチウム二次電池負極用材料が得られる。700℃以上 1500℃以下での熱処理は、捏合物中の炭素質バインダーに含まれる揮発成分

を飛散させ、かつ炭素質バインダーを炭化させるものである。その温度は、炭素質バインダーの種類に併せて、上記温度範囲内で適切な温度を設定すれば良い。この加熱温度が 700℃より低いと、炭素質バインダーを十分に炭化しにくい。また、1500℃より高くても良いが、1500℃程度あれば、炭素質バインダーの揮発成分はほぼ飛散するので、炭化の目的をほぼ達成することができる 1500℃程度で充分である。この炭化処理後に得られる粉末を必要に応じた粒度調整を行って、リチウム二次電池負極用炭素材料として用いることができるが、更に、前記の炭化に続いて、或いは炭化に代えて 2400℃以上 3000℃以下の温度で黒鉛化処理することにより、本発明の効果は更に顕著に得られる。即ち、この温度領域での熱処理により、黒鉛の純化と炭素質バインダーの黒鉛化が同時に進行し、これらにより放電容量の更なる増加が得られる。この黒鉛化温度が 2400℃未満では、炭素質バインダーの黒鉛化が十分に進まず、処理の効果である放電容量の増加は十分に得られない。また、3000℃より高くても良いが、安全性や経済性から 3000℃以下で充分である。

【0031】また、本発明では、上記要件（6）に加えて、前記金属が、鉄、ニッケル、シリコン、コバルトより選ばれた 1 種または 2 種以上の金属であるリチウム二次電池負極用黒鉛の製造方法であることが好ましい。

【0032】炭素は、高温において多くの金属と熔融状態をとる。一般に、これを冷却すると、炭素の溶解限界濃度が減少することから、黒鉛として析出する。その析出の温度や量は、用いる金属種により大きく異なり、例えば、ニッケルは 2000℃において、約 20 原子％の炭素を含む熔融状態を取り得、これを 1500℃まで冷却した際に前記 20 原子％の内、約 7 原子％に相当する炭素が黒鉛として析出する。金属種によっては、高温において液体状態になっても、炭素をほとんど溶解しないものや、また、溶解しても黒鉛として析出しないものがあり、これらは本発明の金属として用いるに適さない。即ち、少なくとも鉄、ニッケル、シリコン、コバルトと炭素を、所定量混合した試料を不活性雰囲気下で高温加熱し、冷却することにより得られる黒鉛を処理して、上記要件（3）を満たす製造を行うことにより得られる材料は、リチウム二次電池負極として優れた特性を有する。

【0033】また、本発明は、上記要件（6）に加えて、前記金属と炭素の熔融状態が、製鉄プロセスの熔融鉄における鉄と炭素の熔融状態であることを特徴とするリチウム二次電池負極用黒鉛の製造方法であっても良い。鉄は、2500℃において、約 25 原子％の炭素を含む熔融状態を取り得、これを冷却した場合に、その溶解限界量は低下し、これを越えた炭素が黒鉛として析出する。製鉄プロセスにおいては、製鉄工程にて炭素を含んだ高温熔融反応物が得られ、その反応物の運搬及び精

製等の工程にて、反応物温度が下がり炭素が析出し、その多くが製鉄ダスト及び製鋼ダストとして回収されている。該ダスト中の炭素濃度は、回収段階で40～60質量%程度である。上記要件(2)のリチウム二次電池負極用黒鉛の製造方法において、原料として該ダストを用いることが、その生成原理から見て可能である。また、現実の工業プロセスから大量に産出する原料を得ることができ、該プロセスで原料を得ることが、その物性安定化や経済性の点で優れた方法である。即ち、該ダストを処理して上記要件(3)を満たす製造を行うことにより得られる材料は、リチウム二次電池負極として優れた特性を有する。

【0034】また、本発明は、上記要件(6)に加えて、前記黒鉛の平均粒径が3μm以上30μm以下であることを特徴とするリチウム二次電池負極用材料の製造方法であることが好ましい。これは、本発明の捏合処理が、粒子の造粒を行うことから、その処理前の原料粒径により、最終的に生成する材料の粒径も大きな影響を受ける。リチウム二次電池負極用材料としての望ましい平均粒径は、5μm以上100μm未満、望ましくは5～50μmの範囲である。この範囲外では、負極材料としての性能、使用性の点で劣る。原料黒鉛の平均粒径が3μm以上30μm以下とすることにより、適正な捏合の条件にて、望ましい粒度範囲の製品が得られることがわかった。

【0035】さらに、本発明は、上記要件(6)に加えて、前記捏合物が、前記黒鉛と前記炭素質バインダーを捏合し、前記炭素質バインダーの軟化点以上の温度に加熱しながら、攪拌、捏合したものであるリチウム二次電池負極用材料の製造方法であることが好ましい。黒鉛と炭素質バインダーを混合、攪拌しながら、加熱を行うことにより、本発明の捏合が進行し得るが、この際の加熱温度は、炭素質バインダーの軟化点以上でないと、捏合及び黒鉛の粒子の造粒はほとんど進行しないため、良好なリチウム二次電池負極用材料は得られない。

【0036】また、本発明は、上記要件(6)に加えて、前記黒鉛と前記炭素質バインダーの捏合割合が、黒鉛100質量部に対して、炭素質バインダーが10～70質量部であるリチウム二次電池負極用材料の製造方法であることが好ましい。この黒鉛と炭素質バインダーの捏合割合が、10質量部未満では、天然黒鉛同士の接着性能が低下するので好ましくなく、また、70質量部を超えると、得られる捏合物中の炭素質バインダーの製品における寄与率が大きくなり、放電容量の低下が誘引されるため好ましくない。

【0037】さらに、本発明は、正極活物質、負極活物質及び非水系電解質を含有するリチウム二次電池において、上記要件(1)～(5)の、少なくとも何れかを満たす材料を負極活物質に含んでなることを特徴とするリチウム二次電池である。上記要件(1)～(5)の材料

は、リチウム二次電池負極として優れた特性を持ち、これを負極活物質として用いて、リチウム二次電池を製造した場合、負極活物質が、従来材料の負極活物質に比べて、高容量等優れた性質を有するため、より高性能のリチウム二次電池が得られる。また、必要に応じて他の負極活物質と混合しても、本発明の効果である高い放電容量等の効果が得られる。

【0038】本発明のリチウム二次電池負極用材料を活物質に用いて負極を形成する方法としては、本発明のリチウム二次電池負極用材料の性能を十分に引き出し且つ、賦形性が高く、化学的、電気化学的に安定であれば、何らこれを制限するものではない。例示すると、本発明のリチウム二次電池負極用材料に、ポリテトラフルオロエチレン等フッ素系樹脂の粉末あるいはディスパージョン溶液を添加後、混合、混練する方法がある。また、本発明のリチウム二次電池負極用材料にポリフッ化ビニリデン(PVdF)等のフッ素系樹脂粉末あるいはカルボキシルメチルセルロース等の水溶性粘結剤を炭素質バインダーにして、N-メチルピロリドン(NMP)、ジメチルホルムアミド、あるいは水、アルコール等の溶媒を用いて、混合することにより、スラリーを作成し、集電体上に塗布、乾燥することにより、成型することもできる。

【0039】本発明の負極活物質は、正極活物質と非水系電解質(例えば、有機溶媒系電解質)と適宜に組み合わせ用いることができるが、これらの非水系電解質(例えば、有機溶媒系電解質)や正極活物質は、リチウム二次電池に通常用いることのできるものであれば、特にこれを制限するものではない。

【0040】正極活物質としては、例えば、リチウム含有遷移金属酸化物 $LiM(1)_xO_2$ (式中、 x は $0 \leq x \leq 1$ の範囲の数値であり、式中、 $M(1)$ は遷移金属を表し、Co、Ni、Mn、Ti、Cr、V、Fe、Zn、Al、Sn、Inのうち少なくとも1種類からなる)、或いは、 $LiM(1)_yM(2)_{2-y}O_4$ (式中、 y は $0 \leq y \leq 1$ の範囲の数値であり、式中、 $M(1)$ 、 $M(2)$ は遷移金属を表し、Co、Ni、Mn、Ti、Cr、V、Fe、Zn、Al、Sn、Inのうち少なくとも1種類からなる)、遷移金属カルコゲン化合物(TiS₂、NbSe₃、等)、バナジウム酸化物(V₂O₅、V₆O₁₃、V₂O₄、V₃O₈、等)及びそのリチウム化合物、一般式 $M_xMo_6C_{h-y}$ (式中、 x は $0 \leq x \leq 4$ 、 y は $0 \leq y \leq 1$ の範囲の数値であり、式中、 M は遷移金属をはじめとする金属、 Ch はカルコゲン元素を表す)で表されるシュブレル相化合物、或いは活性炭、活性炭素繊維、等を用いることができる。

【0041】非水系電解質(例えば、有機溶媒系電解質)における有機溶媒としては、特に制限されるものではないが、例えば、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、クロロエチレン

カーボネート、ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート、1, 1-ジメトキシエタン、1, 2-ジメトキシエタン、1, 2-ジエトキシエタン、γ-ブチロラクトン、テトラヒドロフラン、2-メチルテトラヒドロフラン、1, 3-ジオキサラン、4-メチル-1, 3-ジオキサラン、アニソール、ジエチルエーテル、スルホラン、メチルスルホラン、アセトニトリル、クロロニトリル、プロピオニトリル、ホウ酸トリメチル、ケイ酸テトラメチル、ニトロメタン、ジメチルホルムアミド、N-メチルピロリドン、酢酸エチル、トリメチルオルトホルメート、ニトロベンゼン、塩化ベンゾイル、臭化ベンゾイル、テトラヒドロチオフェン、ジメチルスルホキシド、3-メチル-2-オキサゾリドン、エチレングリコール、サルファイト、ジメチルスルファイト、等の単独もしくは2種類以上の混合溶媒が使用できる。

【0042】電解質としては、従来より公知のものを何れも使用することができ、例えば、 LiClO_4 、 LiBF_4 、 LiPF_6 、 LiAsF_6 、 $\text{LiB}(\text{C}_6\text{H}_5)_4$ 、 LiCl 、 LiBr 、 LiCF_3SO_3 、 $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ 、 $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$ 、 $\text{Li}(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{N}$ 、 $\text{Li}(\text{CF}_3\text{CF}_2\text{CH}_2\text{OSO}_2)_2\text{N}$ 、 $\text{Li}(\text{HCF}_2\text{CF}_2\text{CH}_2\text{OSO}_2)_2\text{N}$ 、 $\text{Li}(\text{C}_6\text{H}_5)_2\text{CHOSO}_2)_2\text{N}$ 、 $\text{LiB}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4$ 、等の1種または2種以上の混合物を挙げることができる。

【0043】以上のように、本発明により、リチウム二次電池負極用材料として、天然黒鉛等の鱗片状黒鉛の最高水準の放電容量、もしくは黒鉛構造から決定される理論容量と同程度の放電容量を持つと共に、かつ、充電初期における副反応に起因する不可逆容量が小さく、大きな充放電電流下で使用した場合でも高い放電容量が得られる、等の優れた特性を示し、鱗片状黒鉛の問題を解決したリチウム二次電池負極用材料、およびその製造方法、並びにこれを用いたリチウム二次電池が工業的に提供されるに至った。

【0044】

【実施例】以下に本発明において、リチウム二次電池負極用材料の構造、製造法の規定に用いた各種物性値の表現方法、測定方法を示す。

【0045】(1) 黒鉛化度 (d_{002} 、 L_c)
単色のX線を平行ビームにコリメートし、高純度シリコンを内部標準として加えた炭素粉末に照射し、黒鉛の(002)面に対応するピークを測定する。そのピークの位置及び半値幅を、内部標準のシリコンのピークを標準として補正することにより、層面間の間隔 d_{002} 及び結晶子のC軸方向の大きさ L_c を算出する。具体的な評価方法は、日本学術振興会第117委員会にて規定されているものに準拠した。

【0046】(2) 比表面積

窒素ガス吸着によるBET法によって測定した。

【0047】(3) 電極作製及び電極性能測定
ポリフッ化ビニリデンのNMP (N-メチル-2-ピロリドン) 溶液に、リチウム二次電池負極用材料粉末とポリフッ化ビニリデンが質量比で95対5となるように加えて混練し、これを厚さ20 μm の銅箔に塗布して、負極電極箔を得た。この負極電極箔を、80℃で乾燥してNMPを蒸発させた後、10mm角に切り出して、負極電極を作成した。この負極電極単極での電極特性を評価するために、対極、参照極にリチウム金属を用いた三極式セルを用いた。電解液には、エチレンカーボネートとジエチルカーボネートの混合溶媒 (体積比で1:1混合) に、 LiClO_4 を1mol/lの割合で溶解したものをを用いた。充放電試験に関しては、電位規制の下、充電、放電共に定電流密度 (0.1 mA/cm^2) で行なった。電位範囲は、0Vから1.5V (リチウム金属基準) とした。初回充電容量、初回放電容量、初期充放電効率を測定すると共に、2回目以後の充放電における放電容量の変化の程度でサイクル特性を評価した。

【0048】(実施例1) コークス粉末4kgと鉄粉末12kgを混合した後、黒鉛容器に入れ、これをタンマン炉でアルゴン気流中で2000℃に昇温加熱し、冷却した。反応後に固形反応物を得た後、その表面部に析出した粒状化合物約1kgを回収した。これを濃塩酸10リットルに入れ、室温で10時間保持した後に濾過し、さらにこれを多量の水で洗浄濾過した後、大気中120℃で20時間乾燥して、中間生成物600gを得た。得られた中間生成物である粉末をジェットミルにて粉碎し、空気分級機にて分級して、平均粒径15 μm の粉末生成物400gを得た。この生成物の化学分析による金属不純物の総計は、1.2質量%であった。また、この粉末生成物の黒鉛化度は、 $d_{002}=0.3355\text{nm}$ 、 $L_c>100\text{nm}$ であり、高い黒鉛化度を有していた。

【0049】この粉末黒鉛300gに対し、コールターピッチ (軟化点80℃) 100gを混合し、200℃、120分間、Z型ニーダーで捏合した。次第に粘度を増し、造粒状態となった造粒物を冷却後解砕し、黒鉛製の坩堝に入れ、リードハンマータイプの連続焼成炉中、800℃の温度で炭素化した。更に、これを黒鉛製の坩堝に入れ、アチソンタイプの黒鉛化炉中3000℃で熱処理、黒鉛化した後、解砕、空気分級により、平均粒径27 μm の生成物320gを得た。

【0050】得られた生成物の黒鉛化度は、 $d_{002}=0.3355\text{nm}$ 、 $L_c>100\text{nm}$ 、比表面積は1.0 m^2/g 、20回タップ時のタップ密度が0.73 g/cm^3 、300回タップ時のタップ密度が1.04 g/cm^3 であった。また、得られた生成物の化学分析による金属不純物の総計は、0.2質量%であった。

【0051】この材料の充放電特性は、初回充電容量が384 mAh/g 、初回放電容量が368 mAh/g

で、初期充放電効率は96%という結果が得られた。また、2回目以後の充放電においても、放電容量はほとんど変わらず、優れたサイクル特性を示すなど、高い電極性能を有していた。

【0052】（実施例2）製鉄プロセスの製鋼ダストとして粉末2kgを回収した。これを濃塩酸10リットルに入れ、室温で12時間保持した後に濾過し、さらにこれを多量の水で洗浄濾過した後、120℃で12時間乾燥した。得られた中間生成物粉末をジェットミルにて粉碎し、空気分級機にて分級して、平均粒径10μmの粉末生成物800gを得た。この生成物の化学分析による金属不純物の総計は、2.1質量%であった。また、この粉末生成物の黒鉛化度は、 $d_{002}=0.3354\text{ nm}$ 、 $L_c>100\text{ nm}$ であり、高い黒鉛化度を有していた。

【0053】この粉末黒鉛400gに対し、コールタールピッチ（軟化点80℃）120gを混合し、200℃、120分間、Z型ニーダーで捏合した。次第に粘度を増し、造粒状態となった造粒物を冷却後解砕し、黒鉛製の坩堝に入れ、リードハンマータイプの連続焼成炉中、800℃の温度で炭素化した。更に、これを黒鉛製の坩堝に入れ、アチソンタイプの黒鉛化炉中3000℃で熱処理、黒鉛化した後、解砕、空気分級により、平均粒径25μmの生成物380gを得た。

【0054】得られた生成物の黒鉛化度は、 $d_{002}=0.3355\text{ nm}$ 、 $L_c>100\text{ nm}$ 、比表面積は0.8m²/g、20回タップ時のタップ密度が0.96g/cm³、300回タップ時のタップ密度が1.14g/cm³であった。また、得られた生成物の化学分析による金属不純物の総計は、0.1質量%であった。

【0055】この材料の充放電特性は、初回充電容量が387mAh/g、初回放電容量が371mAh/gで、初期充放電効率は96%という結果が得られた。また、2回目以後の充放電においても、放電容量はほとんど変わらず、優れたサイクル特性を示すなど、高い電極性能を有していた。

【0056】（実施例3）製鉄プロセスの製鋼ダストとして粉末10kgを回収した。これを濃塩酸50リットルに入れ、室温で12時間保持した後に濾過し、さらにこれを多量の水で洗浄濾過した後、120℃で12時間乾燥した。得られた粉末をジェットミルで粉碎した後に空気分級を行って、平均粒径12μmの粉末生成物3.6kgを得た。この生成物の化学分析による金属不純物の総計は、2.1質量%であった。また、この粉末生成物の黒鉛化度は、 $d_{002}=0.3356\text{ nm}$ 、 $L_c>100\text{ nm}$ であり、高い黒鉛化度を有していた。

【0057】この粉末黒鉛2kgに対し、コールタールピッチ（軟化点80℃）0.66kgを混合し、200℃、120分間、Z型ニーダーで捏合した。次第に粘度を増し、造粒状態となった造粒物を冷却後解砕し、黒鉛

製の坩堝に入れ、マッフル炉を用いて、アルゴン雰囲気下1400℃の温度で炭素化した。更にこれを解砕、空気分級し、平均粒径26μmの生成物1.8kgを得た。

【0058】得られた生成物の黒鉛化度は、 $d_{002}=0.3356\text{ nm}$ 、 $L_c>100\text{ nm}$ 、比表面積は1.2m²/g、20回タップ時のタップ密度が0.72g/cm³、300回タップ時のタップ密度が0.97g/cm³であった。また、得られた生成物の化学分析による金属不純物の総計は、0.5質量%であった。

【0059】この材料の充放電特性は、初回充電容量が373mAh/g、初回放電容量が354mAh/gで、初期充放電効率は95%という結果が得られた。また、2回目以後の充放電においても、放電容量はほとんど変わらず、優れたサイクル特性を示すなど、高い電極性能を有していた。

【0060】（実施例4）コークス粉末3kgとニッケル粉末12kgを混合した後、黒鉛容器に入れ、これをタンマン炉でアルゴン気流中2200℃に昇温加熱し、冷却した。反応後に固形反応物を得た後、その表面部に析出した粒状化合物約750gを回収した。これを濃硝酸とフッ酸の1:1混合溶液1リットルに入れ、室温で12時間保持した後に濾過し、さらに、これを多量の水で洗浄濾過した後、120℃で12時間乾燥した。得られた粉末をジェットミルで粉碎した後、篩分級して平均粒径12μmの粉末生成物370gを得た。この生成物の化学分析による金属不純物の総計は、1.9質量%であった。また、この粉末生成物の黒鉛化度は、 $d_{002}=0.3355\text{ nm}$ 、 $L_c>100\text{ nm}$ であり、高い黒鉛化度を有していた。

【0061】この粉末黒鉛300gに対し、コールタールピッチ（軟化点80℃）150gを混合し、200℃、120分間、Z型ニーダーで捏合した。次第に粘度を増し、造粒状態となった造粒物を冷却後解砕し、黒鉛製の坩堝に入れ、リードハンマータイプの連続焼成炉中、800℃の温度で炭素化した。更に、これを黒鉛製の坩堝に入れ、アチソンタイプの黒鉛化炉中3000℃で熱処理、黒鉛化した後、解砕、空気分級により、平均粒径25μmの生成物290gを得た。

【0062】得られた生成物の黒鉛化度は、 $d_{002}=0.3355\text{ nm}$ 、 $L_c>100\text{ nm}$ 、比表面積は1.1m²/g、20回タップ時のタップ密度が0.74g/cm³、300回タップ時のタップ密度が0.97g/cm³であった。また、得られた生成物の化学分析による金属不純物の総計は、0.6質量%であった。

【0063】この材料の充放電特性は、初回充電容量が386mAh/g、初回放電容量が370mAh/gで、初期充放電効率は96%という結果が得られた。また、2回目以後の充放電においても、放電容量はほとんど変わらず、優れたサイクル特性を示すなど、高い電極

性能を有していた。

【0064】（実施例5）コークス粉末1kgとシリコン粉末8kgを混合した後、黒鉛容器に入れ、これをタンマン炉でアルゴン気流中で2500℃に昇温加熱し、冷却した。反応後に固形反応物を得た後、その表面部に析出した粒状化合物約600gを回収した。これを濃硝酸とフッ酸の1:1混合溶液1リットルに入れ、室温で12時間保持した後に濾過し、さらに、これを多量の水で洗浄濾過した後、120℃で12時間乾燥した。得られた粉末をボールミルで粉砕した後、篩分級して平均粒径15μmの粉末生成物350gを得た。この生成物の化学分析による金属不純物の総計は、7.5質量%であった。

【0065】この粉末黒鉛300gに対し、コールタールピッチ（軟化点80℃）90gを混合し、200℃、120分間、Z型ニーダーで捏合した。次第に粘度を増し、造粒状態となった造粒物を冷却後解砕し、黒鉛製の坩堝に入れ、リードハンマータイプの連続焼成炉中800℃の温度で炭素化した。更に、これを黒鉛製の坩堝に入れ、アチソンタイプの黒鉛化炉中3000℃で熱処理、黒鉛化した後、解砕、空気分級により、平均粒径22μmの生成物370gを得た。

【0066】得られた生成物の黒鉛化度は、 $d_{002}=0.3355\text{nm}$ 、 $L_c>100\text{nm}$ 、比表面積は $1.0\text{m}^2/\text{g}$ 、20回タップ時のタップ密度が $0.96\text{g}/\text{cm}^3$ 、300回タップ時のタップ密度が $1.14\text{g}/\text{cm}^3$ であった。また、得られた生成物の化学分析による金属不純物の総計は、0.1質量%であった。

【0067】この材料の充放電特性は、初回充電容量が $380\text{mAh}/\text{g}$ 、初回放電容量が $361\text{mAh}/\text{g}$ で、初期充放電効率は95%という結果が得られた。また、2回目以後の充放電においても、放電容量はほとんど変わらず、優れたサイクル特性を示すなど、高い電極性能を有していた。

【0068】（実施例6）コークス粉末2kgとコバルト粉末8kgを混合した後、黒鉛容器に入れ、これをタンマン炉でアルゴン気流中で2200℃に昇温加熱し、冷却した。反応後に固形反応物を得た後、その表面部に析出した粒状化合物約400gを回収した。これを濃硝酸とフッ酸の1:1混合溶液1リットルに入れ、室温で12時間保持した後に濾過し、さらにこれを多量の水で洗浄濾過した後、120℃12時間乾燥した。得られた粉末をジェットミルで粉砕した後、篩分級して平均粒径38μmの粉末生成物5gを得た。この生成物の化学分析による金属不純物の総計は、1.5質量%であった。

【0069】このようにして調製した炭素材200gに対し、コールタールピッチ（軟化点80℃）67gを混合し、以下実施例1と同様の手法により、炭化、黒鉛化、解砕、分級を行い、平均粒径25μmの生成物220gを得た。

【0070】得られた生成物の黒鉛化度は、 $d_{002}=0.3355\text{nm}$ 、 $L_c>100\text{nm}$ 、比表面積は $1.0\text{m}^2/\text{g}$ 、20回タップ時のタップ密度が $0.73\text{g}/\text{cm}^3$ 、300回タップ時のタップ密度が $0.98\text{g}/\text{cm}^3$ であった。また、得られた生成物の化学分析による金属不純物の総計は、0.1質量%であった。

【0071】この材料の充放電特性は、初回充電容量が $376\text{mAh}/\text{g}$ 、初回放電容量が $360\text{mAh}/\text{g}$ で、初期充放電効率は96%という結果が得られた。また、2回目以後の充放電においても、放電容量はほとんど変わらず、優れたサイクル特性を示すなど、高い電極性能を有していた。

【0072】（比較例1）天然黒鉛をボールミルにて粉砕した後篩分級し、平均粒径15μmの粉末を得た。この黒鉛の金属不純物の総計は、0.4質量%であり、黒鉛化度は、 $d_{002}=0.3355\text{nm}$ 、 $L_c>100\text{nm}$ と高い黒鉛化度を有していた。この天然黒鉛粉末300gに対し、コールタールピッチ（軟化点80℃）を50gを混合し、200℃、120分間、Z型ニーダーで捏合した。次第に粘度を増し、造粒状態となった造粒物を冷却後解砕し、黒鉛製の坩堝に入れ、リードハンマータイプの連続焼成炉中800℃の温度で炭素化した。これを平均粒径25μmに粒度調製し、黒鉛製坩堝に入れ、アチソンタイプの黒鉛化炉中3000℃で熱処理、黒鉛化した。

【0073】得られた生成物の黒鉛化度は、 $d_{002}=0.3355\text{nm}$ 、 $L_c>100\text{nm}$ 、比表面積は $1.7\text{m}^2/\text{g}$ 、20回タップ時のタップ密度が $0.68\text{g}/\text{cm}^3$ 、300回タップ時のタップ密度が $0.77\text{g}/\text{cm}^3$ であった。また、得られた生成物の化学分析による金属不純物の総計は、0.1質量%であった。

【0074】この材料の充放電特性は、初回充電容量が $390\text{mAh}/\text{g}$ 、初回放電容量が $345\text{mAh}/\text{g}$ で、初期充放電効率は88%という結果であった。

【0075】（比較例2）実施例2と同じ製鉄プロセスの製鋼ダスト2kgを回収した。これを実施例2と同様の方法で、濃塩酸洗浄、水洗浄、乾燥、粉砕、分級を行って、平均粒径10μmの粉末生成物800gを得た。この生成物の化学分析による金属不純物の総計は、2.2質量%であった。また、この粉末生成物の黒鉛化度は、 $d_{002}=0.3356\text{nm}$ 、 $L_c>100\text{nm}$ であり、高い黒鉛化度を有していた。

【0076】この粉末黒鉛400gに対し、コールタールピッチ（軟化点80℃）120gを混合し、200℃、120分間、Z型ニーダーで捏合した。次第に粘度を増し、造粒状態となった造粒物を冷却後解砕し、黒鉛製の坩堝に入れ、実験炉にて窒素雰囲気中600℃の温度で、熱処理を行った。更にこれを、解砕、空気分級により、平均粒径25μmの生成物480gを得た。

【0077】得られた生成物の黒鉛化度は、 $d_{002}=$

0.3360 nm、 $L_c > 100$ nm、比表面積は $11 \text{ m}^2/\text{g}$ 、20回タップ時のタップ密度が $0.56 \text{ g}/\text{cm}^3$ 、300回タップ時のタップ密度が $0.70 \text{ g}/\text{cm}^3$ であった。また、得られた生成物の化学分析による金属不純物の総計は、2.1質量%であった。

【0078】この材料の充放電特性は、初回充電容量が $349 \text{ mAh}/\text{g}$ 、初回放電容量が $297 \text{ mAh}/\text{g}$ で、初期充放電効率は85%という結果が得られた。また、2回目以降の充放電において、放電容量が徐々に減少し、30回の充放電後では、第1回目の放電容量に比べて20%程度の劣化が認められた。

【0079】比較例1、2で得られた黒鉛材の性能を、実施例1～6と比較すると、本発明の黒鉛材の方が、放電容量、初期充放電効率、サイクル特性の電極特性は優

れていることが分かる。

【0080】

【発明の効果】本発明により、リチウム二次電池負極用炭素材料として、天然黒鉛等の鱗片状黒鉛の最高水準の放電容量、もしくは黒鉛構造から決定される理論容量と同程度の放電容量を持つと共に、かつ充電初期における副反応に起因する不可逆容量が大きく、大きな充放電電流下で使用した場合に高い放電容量が得られない等の鱗片状黒鉛の問題を解決したリチウム二次電池負極用材料およびその製造方法が提供された。また、高容量で充放電効率の高い負極材料を用いた本発明のリチウム二次電池により、携帯機器等のさらなる小型・軽量化や長時間の使用が可能となった。

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(54) NEGATIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY, ITS MANUFACTURING METHOD, AND LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative electrode material having a discharge capacity of the highest level of flake graphite such as natural graphite or the discharge capacity equivalent to the theoretical capacity depending on graphite structure, and solving such a problem of the flake graphite that irreversible capacity caused by side reaction in the initial stage of charge is large and discharge capacity in use under high charge/discharge current is low, and to provide the manufacturing method of the negative electrode material, and industrially provide a lithium secondary battery using the negative electrode material.

SOLUTION: A carbon material is obtained by heat treating a kneaded material of graphite prepared by treating carbon deposited in a cooling process of molten state metal and carbon and having a carbon content of 90 mass percent or more and a carbonaceous binder, and this carbon material having a specified range of average particle size and a specified range of tap densities is manufactured as the negative electrode material for the lithium secondary battery, and the lithium secondary battery is manufactured by using this carbon material as the negative electrode active material.

CLAIMS

[Claim(s)]

[Claim 1] The charge of lithium secondary battery negative-electrode material to which the carbon content which processes the carbon which deposited in the cooling process of the melting condition of a metal and carbon, and is obtained is the carbon material which comes to heat-treat the graphite more than 90 mass %, and kneaded material with a carbonaceous binder, and mean particle diameter of this carbon material is characterized 5-micrometer or more and less than 100 micrometers, and the tap density at the time of the 20 times tap being 0.70 g/cm^3 or more .

[Claim 2] The charge of lithium secondary battery negative-electrode material according to claim 1 characterized by the carbonaceous binder of said kneaded material being a carbonization object by heat treatment.

[Claim 3] The charge of lithium secondary battery negative-electrode material according to claim 1 to which said carbon material is characterized by being a graphitization object.

[Claim 4] The charge of lithium secondary battery negative-electrode material given in any 1 term of claims 1-3 characterized by the tap density at the time of the 300 times tap of said carbon material being 0.85 g/cm^3 or more .

[Claim 5] The charge of lithium secondary battery negative-electrode material given in any 1 term of claims 1-4 characterized by a specific surface area according to a BET adsorption method being below $5 \text{ m}^2/\text{g}$ the carbon content of said carbon material above 99 mass %.

[Claim 6] After performing high grade-ized processing until a carbon content becomes about the carbon which deposited in the cooling process of the melting condition of a metal and carbon more than 90 mass % The graphite obtained by performing grinding and air classification using the grinder chosen from the impeller mill, the jet mill, the lei monde mill, or the ball mill, The manufacture approach of the charge of lithium secondary battery negative-electrode material characterized by ****(ing) a carbonaceous binder and graphitizing this kneaded material by $700\text{-}1500 \text{ }^\circ\text{C}$ and/or carbonization at $2400\text{-}3000 \text{ }^\circ\text{C}$.

[Claim 7] Said metal is the manufacture approach of the charge of lithium secondary battery negative-electrode material according to claim 6 characterized by being one sort or two sorts or more of metals chosen from the group which consists of iron, nickel, silicon, and cobalt.

[Claim 8] The manufacture approach of the charge of lithium secondary battery negative-electrode material according to claim 6 that the melting condition of a metal and carbon is characterized by being in the melting condition of iron and carbon in the melting pig iron of an iron-manufacture process.

[Claim 9] The manufacture approach of the charge of lithium secondary battery negative-electrode material given in any 1 term of claims 6-8 to which mean particle diameter of said graphite is characterized by 3-micrometer or more being 30 micrometers or less.

[Claim 10] The manufacture approach of the charge of lithium secondary battery negative-electrode material given in any 1 term of claims 6-9 characterized by agitating and ****(ing) said graphite and said carbonaceous binder, heating to the temperature more than the softening temperature of this carbonaceous binder.

[Claim 11] The manufacture approach of the charge of lithium secondary battery negative-electrode material given in any 1 term of claims 6-10 to which the **** rate of said graphite and said carbonaceous binder is characterized by a carbonaceous binder being 10 - 70 mass section to the graphite 100 mass section.

[Claim 12] The lithium secondary battery which comes to contain positive active material, the negative-electrode active material which comes to contain the charge of lithium secondary battery

negative-electrode material given in any 1 term of claims 1-5, and a nonaqueous electrolyte.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the negative-electrode active material used for the lithium secondary battery and this using insertion of a lithium and an elimination reaction. Discharge capacity is related with the negative-electrode active material greatly used for a highly efficient lithium secondary battery and this highly efficient with few capacity losses at the time of charge and discharge in more detail.

[0002]

[Description of the Prior Art] The lithium secondary battery using carbon materials, such as a graphite, as a negative electrode does not have the dendrite generation at the time of the charge which poses a problem, when a metal lithium is used, and it is actively studied from it being a reliable cell. By forming the so-called graphite lamellar compound which the lithium inserted between graphite layers at the time of charge, especially when a graphite is used as a carbon material the case where occlusion of the lithium was carried out into the negative electrode at the time of charge, the generation of a dendrite which poses a problem was inhibited when a metal lithium was used for a negative-electrode ingredient, and discharge potential also uses a metal lithium -- comparing -- 0-0.1 -- in order [that it is / about V / high] not to be alike too much, it has the outstanding property that high electromotive force is acquired.

[0003] However, that configuration, structure, and the organization of a graphite ingredient and the carbon classified are various, and this difference is reflected in the electrode engine performance.

[0004] When scale-like graphites, such as a natural graphite, are used as a graphite ingredient, it is known compared with the artificial graphite obtained by carrying out graphitization baking of the mesophase microsphere described below, a pitch based carbon fiber, the pitch coke, etc. according to the graphite crystal structure which progressed highly that a high discharge capacity will be obtained (for example, 40th cell debate 1D14). However, in a these scale-like graphite, there is a problem that the initial irreversible capacity resulting from the side reaction which advances mainly near the graphite layer structure edge is large, in an initial charge process. In addition, in a natural graphite, since the carbon mesh plane layer is carrying out priority orientation to the specific direction, the diffusion direction of the lithium in an ingredient is limited and, moreover, the diffusion length is very long [these crystal structures]. Therefore, when it is used under a big charge and discharge current, it is thought that it is difficult to obtain a high discharge capacity, and practical constraint is received.

[0005] When the mesophase microsphere extracted and prepared as a graphite ingredient in the phase which the optical anisotropy phase of a mesophase pitch generated spherically is used, and development of the carbon stratification plane after graphitization is inferior compared with a natural graphite, there is a problem that only about 80 - 85% of discharge capacity is obtained compared with theoretical discharge capacity.

[0006] A pitch based carbon fiber is also variously equipped with a property as an artificial graphite by graphitization processing in the temperature field of a super-elevated temperature. And since the many directions where the diffusion direction of a lithium goes to the interior from

a fiber periphery, and the diffusion length are as short as about several micrometers of the one half of the diameter of fiber from a fiber periphery to a fiber axis, The report (J. Electrochemi.Soc., 142, 8, 2564 (1995)) that the powder which ground this carbon fiber had the large diffusion coefficient as compared with other graphitizability ingredients and the heavy-loading property was checked is also carried out. However, even if it makes heat treatment temperature high although the gestalt of fiber is maintained therefore, development of the crystal structure is checked, and since a high grade-ized processing of the pitch for securing that discharge capacity does not become large and the gestalt of fiber and fiber chemically-modified degree etc. is required, there are problems, like as compared with other ingredients, more manufacturing costs are applied in the phase before graphitization processing.

[0007] Pitch coke belongs to the category of a graphitizability ingredient, although the distance between layers of the carbon mesh plane layer near a natural graphite is approached by graphitization processing in the temperature field of a super-elevated temperature, by the optical anisotropic texture which corks have, graphitization does not progress and, as for these crystal structures, the carbon mesh plane layer has not carried out priority orientation to the specific direction for a natural graphite. Therefore, there is no constraint under the current density looked at by scale-like graphites, such as a natural graphite, it is an ingredient very promising as a negative-electrode ingredient for lithium secondary batteries, and research of the former many is made (for example, JP,63-121257,A, JP,1-204361,A, JP,4-206276,A, etc.). However, the discharge capacity of the ultra-high-temperature treatment (2000-3000-°C baking) article of usual pitch coke has the problem that it is low as compared with geometric capacity (372 mAh/g) (<300 mAh/g).

[0008] As mentioned above, in case various graphite ingredients are used as a negative-electrode active material of a lithium secondary battery, in order to obtain a high discharge capacity, the graphite layer structure which developed into altitude is required. There were problems -- for this purpose, when scale-like graphites, such as a natural graphite, are used, initial irreversible capacity is large and a good property is not acquired under a big charge and discharge current. On the other hand, since development extent of the graphite structure was less than a scale-like graphite when a mesophase microsphere, a pitch based carbon fiber, or pitch coke is used, there was a practical problem that a high discharge capacity was not obtained.

[0009]

[Problem(s) to be Solved by the Invention] While this invention has a discharge capacity comparable as the geometric capacity determined as a carbon material for lithium secondary battery negative electrodes from a discharge capacity of the highest level or graphite structures of a scale-like graphite, such as a natural graphite And solved the problem of a scale-like graphite -- the irreversible capacity resulting from the side reaction in the early stages of charge is large, and a discharge capacity high when it is used under a big charge and discharge current is not obtained. It aims at offering industrially the lithium secondary battery which used this for the negative-electrode ingredient for lithium secondary batteries, and its manufacture approach list.

[0010]

[Means for Solving the Problem] The result to which this invention persons considered wholeheartedly the relation of fine-particles properties, such as particle shape of various graphite ingredients, a generation process, structure, and grain size, and electric physical properties, After ****(ing) this with a carbonaceous binder and considering as kneaded material using the carbon which deposited in the cooling process of the melting condition of a metal and carbon, by

performing carbonization and/or graphitization While this could be used as a negative electrode of a lithium secondary battery and the charge of lithium secondary battery negative-electrode material of a parenthesis showed a high discharge capacity, it found out that it was the ingredient which can solve greatly problems, like the irreversible capacity which had become a problem with the scale-like graphite with a big discharge capacity conventionally is large. Based on this knowledge, it came to offer the lithium secondary battery which used this for the carbon material for lithium secondary battery negative electrodes which is excellent in the electrode characteristic as a negative electrode of a lithium secondary battery, and its manufacture approach list.

[0011] Namely, this invention (1) The carbon content which processes the carbon which deposited in the cooling process of the melting condition of a metal and carbon, and is obtained The graphite more than 90 mass %, It is the carbon material which comes to heat-treat kneaded material with a carbonaceous binder. The charge of lithium secondary battery negative-electrode material to which mean particle diameter of this carbon material is characterized by the tap density at the time of 5-micrometer or more less than 100 micrometers and a 20 times tap being three or more [0.70g //cm], (2) The charge of lithium secondary battery negative-electrode material given in (1) characterized by the carbonaceous binder of said kneaded material being a carbonization object by heat treatment, (3) The charge of lithium secondary battery negative-electrode material given in (1) to which said carbon material is characterized by being a graphitization object, (4) said -- a carbon material -- 300 -- a time -- a tap -- the time -- tap density -- 0.85 -- g/cm³ -- more than -- it is -- things -- the description -- ** -- carrying out -- (-- one --) - (-- three --) -- some -- one -- a term -- a publication -- a lithium secondary battery -- a negative electrode -- material -- a charge -- (5) The charge of lithium secondary battery negative-electrode material given in any 1 term of (1) - (4) characterized by a specific surface area according [the carbon content of said carbon material] to a BET adsorption method being below 5m²/g above 99 mass %, (6) After performing high grade-ized processing until a carbon content becomes about the carbon which deposited in the cooling process of the melting condition of a metal and carbon more than 90 mass % The graphite obtained by performing grinding and air classification using the grinder chosen from the impeller mill, the jet mill, the lei monde mill, or the ball mill, The manufacture approach of the charge for lithium secondary batteries of negative-electrode material characterized by ****(ing) a carbonaceous binder and graphitizing this kneaded material at carbonization by 700-1500 °C, and/or graphitizing at 2400-3000 °C (7) said -- a metal -- iron -- nickel -- silicon -- and -- cobalt -- from -- becoming -- a group -- choosing -- having -- one -- a sort -- or -- two -- a sort -- more than -- a metal -- it is -- things -- the description -- ** -- carrying out -- (-- six --) -- a publication -- a lithium secondary battery -- a negative electrode -- material -- a charge -- manufacture -- an approach -- (8) The manufacture approach of the charge of lithium secondary battery negative-electrode material given in (6) that the melting condition of a metal and carbon is characterized by being in the melting condition of iron and carbon in the melting pig iron of an iron-manufacture process, (9) The manufacture approach of the charge of lithium secondary battery negative-electrode material given in any 1 term of (6) - (8) to which mean particle diameter of said graphite is characterized by 3-micrometer or more being 30 micrometers or less, (10) Heating said graphite and said carbonaceous binder to the temperature more than the softening temperature of this carbonaceous binder Churning, The manufacture approach of the charge of lithium secondary battery negative-electrode material given in any 1 term of (6) - (9) characterized by ****(ing) (11) The **** rate of said graphite and said carbonaceous binder receives the graphite 100 mass section. The manufacture approach of the charge of lithium secondary battery negative-electrode

material given in any 1 term of (6) - (10) characterized by a carbonaceous binder being 10 - 70 mass section (12) Positive active material, It is the lithium secondary battery which comes to contain in any 1 term of claims 1-5 the negative-electrode active material which comes to contain the charge of lithium secondary battery negative-electrode material and nonaqueous electrolyte of a publication.

[0012]

[Embodiment of the Invention] Below, the contents of this invention are explained concretely.

[0013] The graphite for lithium secondary battery negative electrodes concerning this invention performs the postheat treatment which the carbon content which processes the carbon which deposited by the cooling process of the melting condition of a metal and carbon, and is obtained ****(ed) the graphite and carbonaceous binder more than 90 mass %, and used as kneaded material, and is a charge of lithium secondary battery negative-electrode material from which mean particle diameter is obtained in this when the tap density at the time of 5-micrometer or more less than 100 micrometers and a 20 times tap prepares to 0.70 g/cm^3 or more.

[0014] As requirements for the graphite for lithium secondary battery negative electrodes of this invention In order to acquire the advanced graphite structure which is equal to a natural graphite about the graphite used in the first place as a raw material though it is an artificial graphite The carbon content of this graphite is controlled in the optimal range to that you make it deposit from a melting condition with a metal, and the second, It is in heat-treating, after ****(ing) this graphite and a carbonaceous binder to the third and considering as kneaded material, and fourth preparing this so that it may become tap density 0.70 g/cm^3 or more at the time of the mean particle diameter of less than 100 micrometers of 5 micrometers or more, and a 20 times tap. All requirements are doubled from the above first to the fourth, and it is called the above-mentioned requirements (1) by the following description.

[0015] In order to acquire the advanced graphite structure which is equal to a natural graphite about the graphite which is the first requirement, and which is used as a raw material though it is an artificial graphite, it explains that you make it deposit from a melting condition with a metal.

[0016] The graphite used as a raw material of the charge of lithium secondary battery negative-electrode material of this invention belongs to an artificial graphite in a partition called the natural graphite and artificial graphite in the generation process. It is most common to heat-treat carbon at a 2000 to 3000 °C elevated temperature finally as an approach of manufacturing an artificial graphite, using the raw material used as a principal component. However, in the artificial graphite obtained when this approach is used, since graphite structure does not fully advance as compared with a natural graphite, a degree of graphitization is inferior. On the other hand, the carbon which deposited by the cooling process of the melting condition of a metal and carbon takes the graphite structure which developed into altitude. This is because a stable graphite is formed thermodynamically, in case carbon deposits from a melting phase. Although the detail of the essential difference in scale-like graphites, such as graphite structure, a natural graphite, etc. which developed into this altitude, is not yet clear, in the electrical order of the graphite for lithium secondary battery negative electrodes of this invention, problems, like the irreversible capacity which had become a problem with scale-like graphites, such as a natural graphite, is large are greatly improvable. As for a natural graphite, in this, a graphite particle consists of a single crystal graphite mostly, and it is presumed to the crystal orientation having become in the about 1 direction that it originates in consisting of graphite polycrystal and moreover the orientation having become in the many directions as compared with a natural

graphite, as for the graphite particle which is the raw material of this invention.

[0017] Moreover, the carbon content used as a raw material which is the second requirement is explained.

[0018] One of the big meaning of using a graphite as a negative-electrode ingredient for lithium secondary batteries is that a discharge curve flat in most use fields on a par with potential [in / in the potential in the reaction which Li ion is inserted between graphite layers at the time of the chemical change of a charge-and-discharge process, i.e., charge, a graphite lamellar compound is formed, and a lithium ion ****s at the time of discharge, and returns to a graphite / change of a lithium metal and a lithium ion] is obtained. The great portion of charge-and-discharge capacity of the lithium secondary battery negative-electrode ingredient obtained by this invention is obtained with the graphite used as a raw material. That is, that a high discharge capacity by which the lithium secondary battery negative-electrode ingredient obtained by this invention is characterized is obtained although a binder component is carbonized or graphitized and contributes to discharge capacity by passing through carbonization and/or graphitization after ****(ing) with a carbonaceous binder originates in a high discharge capacity of the graphite of a raw material itself. Therefore, when the purity of the graphite used as a raw material is low, the rate of a graphite of participating in the charge-and-discharge reaction in the negative-electrode ingredient obtained from it cannot become small, and cannot bear a discharge capacity high as a negative-electrode ingredient. Since the discharge capacity will not reach 335 mAh/g if the content does not have more than 90 mass % at least even if the graphite in a negative-electrode ingredient has the discharge capacity of 372 mAh/g which is the theoretical discharge capacity, The carbon content of the still more desirable graphite from the point that the negative-electrode ingredient of high discharge capacity is not obtained, and a high discharge capacity of 350 or more mAh/g which is not usually attained except scale-like graphites, such as a natural graphite, obtains is more than 95 mass %. As mentioned above, the carbon content of the graphite used as a raw material of the charge of lithium secondary battery negative-electrode material of this invention is desirably specified more than as 95 mass % more than 90 mass %. The graphite with which are satisfied of the range more than carbon concentration 90 mass % is easily obtained independent or by combining and using in refinery processes, such as a floatation process known well industrially, acid treatment, and elevated-temperature heat treatment.

[0019] Moreover, after ****(ing) the graphite and carbonaceous binder which are the third requirement and which are a raw material and considering as kneaded material, it explains heat-treating. First of all, the greatest meaning of this processing is shown in aiming at improvement in the shape of powder somatic [, such as reduction of irreversible capacity, and specific surface area, tap density,] by the proper granulation or the adhesion of a particle by ****, maintaining a high discharge capacity which is equal to the geometric capacity which the graphite used as a raw material has. As a carbonaceous binder, what used carbon, such as pitches, such as a coal-tar pitch, a petroleum pitch, and a naphthalene pitch, 3, 5-dimethylphenol formaldehyde resins, and a polyvinyl chloride, as the principal component is raised, and what fused these, and the thing ground in mean particle diameter of 5-300 micrometers are used. Moreover, this **** is application of an approach which uses graphite powder and a carbonaceous binder as a raw material, and manufactures a precise graphite product and which was conventionally used widely in the carbon material field. If the example is shown, after mixing both, it agitates and **** first, heating. Thereby, the kneaded material of the above-mentioned graphite and a carbonaceous binder, i.e., a bead-like granulation object, is obtained. By

heat-treating this granulation object, the organic substance in a carbonaceous binder is carbonized or graphitized, and it can participate in the adsorption and desorption or insertion desorption of a lithium ion. When not performing this heat treatment, the carbonaceous binder is extremely inferior in the absorptivity-and-desorptivity ability of a lithium ion while not stabilizing it thermally and chemically. In addition, the heat-treated carbonaceous binder enables reduction of side reaction, and an improvement of the shape of powder somatic by the role of granulation of said graphite powder, and adhesion, and its heat treatment proper also in this semantics is indispensable.

[0020] Moreover, the aforementioned kneaded material which is the fourth requirement is explained about preparing the mean particle diameter of less than 100 micrometers of 5 micrometers or more, and the tap density at the time of a 20 times tap so that it may become 0.70 g/cm^3 or more. When mean particle diameter is as small as less than 5 micrometers, and the problem of an ununiformity occurring in the coating side in the increment in the irreversible capacity by the increment in specific surface area, the fall of bulk density, and negative-electrode electrode production was produced, and large and mean particle diameter applies to an electrode foil as a lithium secondary battery negative electrode exceeding 100 micrometers, problems -- required smooth nature is not obtained -- arise. Furthermore, it is more desirable that it is the mean particle diameter of 50 micrometers or less from the ease of carrying out of diffusion of the homogeneity of the reaction in the time of charge and discharge and Li ion inside a particle. The negative-electrode ingredient for lithium secondary batteries which was excellent by performing grinding of kneaded material and grain refining is obtained so that this average size range may be satisfied and the tap density at the time of a 20 times tap may become 0.70 g/cm^3 or more. It explains controlling this tap density in the optimal range. The measuring method of the tap density of a graphite powder ingredient is specified to JIS-K5101, and was measured based on this. Although the tap density of fine particles rises according to that count of a tap about specifying this tap density by 20 times of the counts of a tap, it depends for the stability and operability at the time of electrode manufacture to tap density when there are few counts of a tap strongly. Moreover, although the same definition was possible, from the point of the repeatability of the accuracy of measurement or measured value, it thought that a convention of 20 counts of a tap was the optimal also by convention of the tap density at the time of less than 20 times of taps, and specified here by it. In the graphite as a charge of lithium secondary battery negative-electrode material, it is important also in actuation of transportation of not only making easy stable operation of an electrode foil coating process but an ingredient, storage, etc. to raise tap density. For example, if a mesophase microsphere is compared with a natural graphite with similar particle size distribution, the tap density of a natural graphite is as low as $1/3 - 1/5$, and when this uses a homogeneous quantity of a graphite for accumulating at the time of coating liquid production, the liquid viscosity will produce problems, like become very large and uniform coating becomes difficulty more. It is attained by classifying that performing control of this mean particle diameter and tap density controls to fitness the mean particle diameter and particle size distribution of the graphite used as a raw material of kneaded material, and/or the obtained kneaded material after cooling, grinding and if needed until it becomes a predetermined grain size. As for the average grain size of a raw material graphite, it is desirable to carry out to below the average grain size of the end product made into the purpose, and, as for the particle size at the time of grinding and classifying kneaded material, it is desirable to make it larger than the particle size of the graphite used as a start raw material. If mean particle diameter of the charge

of lithium secondary battery negative-electrode material which is a product is made smaller than the particle size of a start raw material, destruction of the graphite particle which is a start raw material takes place, and it is not desirable on the engine performance. That is, in the charge of lithium secondary battery negative-electrode material of this invention, when the mean particle diameter of less than 100 micrometers of 5 micrometers or more and the tap density at the time of a 20 times tap satisfied 0.70 g/cm^3 or more, it turned out that the difficulty in the case of coating liquid production seen with the natural graphite is avoidable.

[0021] As mentioned above, by satisfying the above-mentioned requirements (1), i.e., all the requirements from said first to the fourth, to coincidence While having a discharge capacity comparable as the geometric capacity determined as a carbon material for lithium secondary battery negative electrodes from a discharge capacity of the highest level or graphite structures of a scale-like graphite, such as a natural graphite And the irreversible capacity resulting from the side reaction in the early stages of charge is small, when it is used under a big charge and discharge current, the property which was [obtain / a high discharge capacity] excellent is acquired, and the charge of lithium secondary battery negative-electrode material which solved the problem of a scale-like graphite came to be offered.

[0022] Furthermore, in addition to the above-mentioned requirements (1), the carbonaceous binder of said kneaded material may be carbide by heat treatment as requirements for the charge of lithium secondary battery negative-electrode material of this invention. This is called the above-mentioned requirements (2) by the following description.

[0023] In order to heat-treat said kneaded material and to carbonize kneaded material, it is desirable to heat-treat under a non-oxidizing atmosphere at 700°C or more temperature of 1500°C or less. Heat treatment at 700°C or more 1500°C or less disperses the volatile component contained in the carbonaceous binder in kneaded material, and carbonizes a brown coal genius binder. The temperature is combined with the class of carbonaceous binder, and should just set up suitable temperature in the above-mentioned temperature requirement. If whenever [this stoving temperature] is lower than 700°C , it will fully be hard to carbonize a carbonaceous binder. Moreover, although it may be higher than 1500°C , if there are about 1500°C , since the volatile component of a binder disperses mostly and the purpose of carbonization can be attained mostly, about 1500°C is enough. That is, in addition to the above-mentioned requirements (1), the ingredient of this invention which used the carbonaceous binder of kneaded material as carbide by heat treatment shows the property which was excellent as a carbon material for lithium secondary battery negative electrodes.

[0024] Moreover, it is desirable that said carbon material is a graphitization object as requirements for the charge of lithium secondary battery negative-electrode material of this invention in addition to the above-mentioned requirements (1). This is called the above-mentioned requirements (3) by the following description. This graphitization object is obtained by graphitizing said kneaded material below 2400°C or more 3000°C , after performing carbonization processing if needed. Although it is desirable to usually perform carbonization processing before graphitization at the temperature of 700°C or more 1500°C or less extent, and to carry out in respect of the operation stability in graphitization processing and safety, if these problems are avoidable, carbonization processing is omissible in order to obtain the target ingredient. That is, the effectiveness of this invention is acquired still more notably by graphitization processing. That is, purification of a graphite and graphitization of a carbonaceous binder advance to coincidence by heat treatment in this temperature field, and the further

increment in discharge capacity is acquired by these. At less than 2400°C, this graphitization temperature does not fully progress and, as for the increment in the discharge capacity which is the effectiveness of processing, graphitization of a carbonaceous binder is not fully acquired for it. Moreover, although it may be higher than 3000 °C, it is enough below 3000 °C from safety or economical efficiency. That is, in addition to the above-mentioned requirements (1), the ingredient obtained by using said carbon material as a graphitization object shows the property which was excellent as a charge of lithium secondary battery negative-electrode material.

[0025] Furthermore, it is desirable that the tap density at the time of a 300 times tap is three or more 0.85 g/cm as requirements for the charge of lithium secondary battery negative-electrode material of this invention in addition to above-mentioned requirements (1) - (3). This is called the above-mentioned requirements (4) by the following description. That is, it is further improved by the property as fine particles by satisfying tap density 0.85 g/cm³ at the time of a 300 times tap in addition to the requirements of 0.70 g/cm³ or more in the tap density at the time of the 20 times tap which specified the above-mentioned requirements (4) on the above-mentioned requirements (1). Although it said that it depends for the stability and operability at the time of electrode manufacture to tap density (this invention prescribes the time of a 20 times tap) when there are few counts of a tap strongly in explanation of a convention of the above-mentioned requirements for this invention (1) After satisfying proper tap density when the fixed range and the count of a tap have little average grain size by specifying the tap density at the time of a 300 times tap further here It finds out acquiring the effectiveness of this invention still more notably by making tap density when there are many counts of a tap accomplish more than fixed. For example, it sets to two kinds of fine particles A and B with the tap density equivalent at three or more 0.70 g/cm at the time of a 20 times tap. Supposing it of less than 0.85 g/cm³ and fine particles B is 0.85 g/cm³ or more, the tap density at the time of the 300 times tap of fine particles A In the operability in the time of slurry production using the solvent in an electrode foil coating process, and the case of the electrode foil press after coating, the stability of that the fine particles B are easier for operability and the manufactured electrode foil is excellent. In the kneading process at the time of slurry production, or the press process after coating, since change to still higher bulk density takes place by making bulk density more than fixed into a starting condition, this is considered that the ease of the change is expressed with the tap density at the time of a 300 times tap. That is, it turned out that the effectiveness of this invention is shown still more notably 300 times if tap density is 0.85 g/cm³ or more .

[0026] Furthermore, in addition to above-mentioned requirements (1) - (4) , carbon content more than 99 mass % and whose specific surface area according to a BET adsorption method is below 5m²/g as requirements for the charge of lithium secondary battery negative-electrode material of this invention is desirable. That is, in addition to above-mentioned requirements (1) - (4), all of raising a carbon content more than a fixed rate and controlling specific surface area below to a fixed value are filled. By the following description, this is called the above-mentioned requirements (5). The carbon content of the charge of lithium secondary battery negative-electrode material which is the factor which constitutes these requirements is explained. Although the discharge capacity obtained as a negative-electrode ingredient becomes large since insertion of a lithium ion and the rate of the graphite structure of participating in desorption are so large that this carbon content is high, it is important for metallic elements, adsorption moisture, etc., such as iron, to lessen elements other than carbon and the content of a compound. When a carbon content is under 99 mass %, problems, such as degradation of nonaqueous

electrolyte and a stability fall of the coating liquid in a coating stroke, arise [the fall of a cycle property or the increment in irreversible capacity according to degradation of the electrolytic solution etc. by the effect of an impurity metal] under the effect of moisture again. In order to reduce these bad influences, a carbon content is preferably carried out to more than 99.5 mass % more than 99 mass %.

[0027] Moreover, similarly a BET specific surface area is explained. As a general index which describes the specific surface area of graphite powder, a BET specific surface area begins this industry, and is widely used by the technical field relevant to carbon and a graphite. This desorbs the adsorbate beforehand, makes nitrogen gas stick to the powder put into the vacuum housing at liquid nitrogen temperature, and is obtained by asking for the isothermal adsorption curve. When the specific surface area by this BET adsorption method $5\text{m}^2/\text{g}$ super-**, in case it is negative-electrode electrode production, or unevenness and an ununiformity part occur in a coating side, adsorption of water in atmospheric air becomes remarkable, and high impurity concentration increases, or deteriorating [of the electrode engine performance] becomes remarkable [that the side reaction in early stages of charge and discharge increases etc.].

[0028] While having a discharge capacity comparable as the geometric capacity determined as a carbon material for lithium secondary battery negative electrodes by satisfying the above requirements from a discharge capacity of the highest level or graphite structures of a scale-like graphite, such as a natural graphite And the irreversible capacity resulting from the side reaction in the early stages of charge was small, when it was used under a big charge and discharge current, the property which was [obtain / a high discharge capacity] excellent was acquired, and it was shown that the negative-electrode ingredient for lithium secondary batteries which solved the problem of a scale-like graphite is offered.

[0029] Next, the manufacture approach of the graphite for lithium secondary battery negative electrodes of above-mentioned this invention is explained.

[0030] Processing of the carbon which deposited in the cooling process of the melting condition of a metal and carbon the manufacture approach of this invention After performing high grade-ized processing until a carbon content reaches more than 90 mass % Grinding and air classification using the grinder chosen from the impeller mill, the jet mill, the lei monde mill, or the ball mill are performed. It is the manufacture approach of the charge of lithium secondary battery negative-electrode material which **** the obtained graphite with a carbonaceous binder and is characterized by graphitizing this kneaded material at carbonization and/or $2400\text{--}3000\text{ }^\circ\text{C}$ by $700\text{--}1500\text{ }^\circ\text{C}$. By the following description, these requirements are called the above-mentioned requirements (6). Namely, the above-mentioned requirements (6) are the purposes which manufacture easily and industrially the outstanding charge of lithium secondary battery negative-electrode material. In case a raw material graphite is obtained first, high grade-ized processing of the carbon which deposited in the cooling process of the melting condition of a metal and carbon is performed. After grinding and air classification using the grinder optimal after considering as the carbon content more than fixed performing grain refining and obtaining kneaded material with a binder by making this into a raw material, it is the manufacture approach characterized by carrying out optimal heat treatment. It is possible to obtain the charge of lithium secondary battery negative-electrode material which has the outstanding property by the manufacture approach of this invention by the easier and high process yield. High grade-ization said here is processing for raising the carbon content of the carbon which deposited in the cooling process of the melting condition of a metal and carbon more than 90 mass %, and is

independent or combining and using about the refinery process generally [a floatation process, acid treatment, elevated-temperature heat treatment, etc.] known. When grinding and grain-size preparation called a classification are performed before performing high grade-ized processing, it is difficult to control the average grain size of the graphite which is a raw material by grain-size change resulting from a great portion of metal particles ****ing in high grade-ized processing etc. Moreover, if it does not grind after high-grade-izing, a product with a predetermined average grain size cannot be obtained by the high yield. Moreover, compared with the case where the graphite which has not passed through grinding is used, improvement in fine-particles characteristic values, such as bulk density of the generated charge of lithium secondary battery negative-electrode material and tap density, can make easily by using the grinder chosen from an impeller mill, a jet mill, a lei monde mill, and a ball mill. As effectiveness which grinds a raw material, the rough edge of the character of the configuration of the scale-like particle which exists immediately after high grade-ized processing is rounded off in a grinding process, it will carry out change more nearly spherically soon, and will depend this on being reflected also in the physical properties of the charge of lithium secondary battery negative-electrode material by which this is manufactured through processings, such as **** with a carbonaceous binder, subsequent carbonization, and graphitization. In this grinding process, changing the configuration of most scale-like particles and making it become a curved-surface configuration particle makes the basis of the above-mentioned requirements (6). In the interior of a grinder, although the grinding phenomenon itself breaks or lacks a particle, when particles repeat contact, a collision, and wear, a phosphorus flaky graphite particle changes to a curved-surface configuration particle, and is presumed that the high fitness as a raw material graphite of the charge of lithium secondary battery negative-electrode material is acquired. After ****(ing) this graphite with a carbonaceous binder and obtaining kneaded material, the charge of lithium secondary battery negative-electrode material made into the purpose is obtained by graphitizing this kneaded material below 700 °C or more 1500 °C below carbonization and/or 2400 °C or more 3000 °C. Heat treatment at 700 °C or more 1500 °C or less disperses the volatile component contained in the carbonaceous binder in kneaded material, and carbonizes a brown coal genius binder. The temperature is combined with the class of carbonaceous binder, and should just set up suitable temperature in the above-mentioned temperature requirement. If whenever [this stoving temperature] is lower than 700 °C, it will fully be hard to carbonize a carbonaceous binder. Moreover, if there are about 1500 °C, since the volatile component of a carbonaceous binder disperses mostly, about 1500 °C which can attain the purpose of carbonization mostly are enough as it, although it may be higher than 1500 °C. Although grain-size [powder / which is obtained after this carbonization processing] preparation if needed can be performed and it can use as a carbon material for lithium secondary battery negative electrodes, the effectiveness of this invention is acquired still more notably by replacing with carbonization and carrying out graphitization processing following the further aforementioned carbonization, at 2400-°C or more temperature of 3000 °C or less. That is, purification of a graphite and graphitization of a carbonaceous binder advance to coincidence by heat treatment in this temperature field, and the further increment in discharge capacity is acquired by these. At less than 2400 °C, this graphitization temperature does not fully progress and, as for the increment in the discharge capacity which is the effectiveness of processing, graphitization of a carbonaceous binder is not fully acquired for it. Moreover, although it may be higher than 3000 °C, it is enough below 3000 °C from safety or economical efficiency.

[0031] Moreover, it is desirable that it is the manufacture approach of the graphite for lithium secondary battery negative electrodes which are one sort or two sorts or more of metals with which said metal was chosen from iron, nickel, silicon, and cobalt in this invention in addition to the above-mentioned requirements (6).

[0032] Carbon takes many metals and melting conditions in an elevated temperature. Generally, if this is cooled, since carbonaceous solubility limit community concentration decreases, it deposits as a graphite. The temperature and the amount of the deposit change greatly with metal kinds to be used, for example, nickel can take the melting condition containing the carbon of about 20 atoms % in 2000 °C, and when this is cooled to 1500 °C, the carbon which is equivalent to about 7 atoms % among said 20 atom %s deposits as a graphite. Even if it will be in a liquid condition in an elevated temperature depending on a metal kind, even if it dissolves, there are what hardly dissolves carbon, and a thing which does not deposit as a graphite, and these are not suitable for using as a metal of this invention again. That is, the ingredient obtained by performing manufacture which processes the graphite which carries out heating at high temperature of the sample which carried out specified quantity mixing of iron, nickel, silicon, cobalt, and the carbon under an inert atmosphere at least, and is obtained by cooling, and satisfies the above-mentioned requirements (3) has the property which was excellent as a lithium secondary battery negative electrode.

[0033] Moreover, this invention may be the manufacture approach of the graphite for lithium secondary battery negative electrodes that the melting condition of said metal and carbon is characterized by being in the melting condition of iron and carbon in the melting pig iron of an iron-manufacture process in addition to the above-mentioned requirements (6). When iron can take the melting condition containing the carbon of about 25 atoms % in 2500 °C and this is cooled, the melting critical mass falls and the carbon beyond this deposits as a graphite. In the iron-manufacture process, the elevated-temperature melting reactant which contained carbon at the iron making process is obtained, at processes, such as conveyance of the reactant, and purification, reactant temperature falls, carbon deposits and the many are collected as iron making dust and steel-manufacture dust. The carbon concentration in this dust is 40 - 60 mass % extent in a recovery phase. In the manufacture approach of the graphite for lithium secondary battery negative electrodes of the above-mentioned requirements (2), it sees from the generation principle and is possible to use this dust as a raw material. Moreover, being able to obtain the raw material produced in large quantities from an actual industrial process, and obtaining a raw material in this process is the approach which was excellent in respect of the physical-properties stabilization and economical efficiency. That is, the ingredient obtained by performing manufacture which processes this dust and satisfies the above-mentioned requirements (3) has the property which was excellent as a lithium secondary battery negative electrode.

[0034] Moreover, as for this invention, it is desirable that it is the manufacture approach of the charge of lithium secondary battery negative-electrode material that the mean diameter of said graphite is characterized by 3-micrometer or more being 30 micrometers or less in addition to the above-mentioned requirements (6). Since **** processing of this invention performs the granulation of a particle, this is influenced also with a big particle size of the ingredient finally generated with the raw material particle size before the processing. The range of 5 micrometers or more less than 100 micrometers of desirable mean particle diameter as a charge of lithium secondary battery negative-electrode material is 5-50 micrometers desirably. this .. if out of range, it is inferior in respect of the engine performance as a negative-electrode ingredient, and usability.

When the mean particle diameter of a raw material graphite sets to 3 micrometers or more 30 micrometers or less showed that the product of a desirable size range was obtained on condition that proper ****.

[0035] Furthermore, while in addition to the above-mentioned requirements (6) said kneaded material **** said graphite and said carbonaceous binder and heats to the temperature more than the softening temperature of said carbonaceous binder, as for this invention, it is desirable that it is the manufacture approach of the charge of lithium secondary battery negative-electrode material of agitating and ****(ing). Although **** of this invention may advance by heating, mixing and agitating a graphite and a carbonaceous binder, since the granulation of the particle of **** and a graphite hardly advances unless whenever [stoving temperature / in this case] is more than the softening temperature of a carbonaceous binder, the good charge of lithium secondary battery negative-electrode material is not obtained.

[0036] Moreover, as for this invention, it is desirable that it is the manufacture approach of the charge of lithium secondary battery negative-electrode material that the **** rate of said graphite and said carbonaceous binder is [a carbonaceous binder] 10 - 70 mass section to the graphite 100 mass section in addition to the above-mentioned requirements (6). Since the adhesive ability of natural graphites falls under in 10 mass sections, the **** rate of this graphite and a carbonaceous binder is not desirable, and if 70 mass sections are exceeded, since the contribution in the product of the carbonaceous binder in the kneaded material obtained becomes large and the fall of discharge capacity is attracted, it is not desirable.

[0037] Furthermore, this invention is a lithium secondary battery characterized by coming to contain in a negative-electrode active material the ingredient of above-mentioned requirements (1) - (5) which fills at least any they are in the lithium secondary battery containing positive active material, a negative-electrode active material, and a nonaqueous electrolyte. The above-mentioned requirements (1) Since a negative-electrode active material has the property excellent in high capacity etc. compared with the negative-electrode active material of an ingredient conventionally when the ingredient of - (5) has the property which was excellent as a lithium secondary battery negative electrode and a lithium secondary battery is manufactured, using this as a negative-electrode active material, the lithium secondary battery of high performance is obtained more. Moreover, even if it mixes with other negative-electrode active materials if needed, effectiveness, such as a high discharge capacity which is the effectiveness of this invention, is acquired.

[0038] As an approach of using the charge of lithium secondary battery negative-electrode material of this invention for an active material, and forming a negative electrode, by fully pulling out the engine performance of the charge of lithium secondary battery negative-electrode material of this invention, if size enlargement nature is high and electrochemically [chemically and] stable, this will not be restricted at all. When it illustrates, the approach of mixing and kneading is in the charge of lithium secondary battery negative-electrode material of this invention after adding the powder or dispersion solution of fluororesin, such as polytetrafluoroethylene. Moreover, it can also cast by creating a slurry, and applying and drying on a charge collector by using water-soluble binders, such as fluororesin powder, such as polyvinylidene fluoride (PVdF), or carboxyl methyl cellulose, as a carbonaceous binder at the charge of lithium secondary battery negative-electrode material of this invention, and mixing using solvents, such as N-methyl pyrrolidone (NMP), dimethylformamide or water, and alcohol.

[0039] Although the negative-electrode active material of this invention can be suitably combined

with positive active material and a nonaqueous electrolyte (for example, organic solvent system electrolyte) and can be used, such nonaqueous electrolytes (for example, organic solvent system electrolyte) or positive active material will not restrict especially this, if it can usually use for a lithium secondary battery.

[0040] As positive active material, it is lithium content transition-metals oxide $\text{LiM}(1)_x\text{O}_2$ (among a formula), for example. x is the numeric value of the range of $0 \leq x \leq 1$, and $M(1)$ expresses transition metals among a formula. or it consists of at least one kind in Co, nickel, Mn, Ti, Cr, V, Fe, Zn, aluminum, Sn, and In $\text{LiM}(1)_y\text{M}(2)_{2-y}\text{O}_4$ (y is the numeric value of the range of $0 \leq y \leq 1$ among a formula) $M(1)$ and $M(2)$ express transition metals among a formula. Co, nickel, Mn, Ti, Consist of at least one kind in Cr, V, Fe, Zn, aluminum, Sn, and In. Transition-metals chalcogen ghasts (TiS_2 , NbSe_3 , etc.), vanadium oxides (V_2O_5 , V_6O_{13} , V_2O_4 , V_3O_8 , etc.), and the lithium compound of those, The SHUBURERU phase compound expressed with general formula $\text{M}_x\text{Mo}_6\text{Ch}_8\text{-y}$ ($0 \leq x \leq 4$ and y of x are the numeric values of the range of $0 \leq y \leq 1$ among a formula, and metals including transition metals and Ch express a chalcogen element among a formula in M) or activated carbon, an activated carbon fiber, etc. can be used.

[0041] As an organic solvent in a nonaqueous electrolyte (for example, organic solvent system electrolyte) Although not restricted especially, for example Propylene carbonate, Ethylene carbonate, butylene carbonate, chloroethylene carbonate, Dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, 1 and 1-dimethoxyethane, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, Gamma-butyrolactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, the 4-methyl -1, 3-dioxolane, an anisole, Diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, Chloro nitril, propionitrile, trimethyl borate, silicic-acid tetramethyl, Nitromethane, dimethylformamide, N-methyl pyrrolidone, ethyl acetate, trimethyl alt.formate, a nitrobenzene, a benzoyl chloride, and bromination -- benzoyl -- Tetrahydrothiophene, dimethyl sulfoxide, 3-methyl-2-oxazolidone, ethylene glycol, an ape fight, a dimethyl ape fight, and independent or two or more kinds of mixed solvents of ** can be used.

[0042] As an electrolyte, each what are better known than before can be used. For example, LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , $\text{LiB}(\text{C}_6\text{H}_5)$, LiCl , LiBr , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$, $\text{Li}(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{CF}_2\text{CH}_2\text{OSO}_2)_2\text{N}$, One sort or two sorts or more of mixture, such as $\text{Li}(\text{HCF}_2\text{CF}_2\text{CH}_2\text{OSO}_2)_2\text{N}$, $\text{Li}[(\text{CF}_3)_2\text{CHOSO}_2]_2\text{N}$, and $\text{LiB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$, can be mentioned.

[0043] As mentioned above, while having a discharge capacity comparable as a discharge capacity of scale-like graphites, such as a natural graphite, of the highest level, or the geometric capacity determined from graphite structure as a charge of lithium secondary battery negative-electrode material by this invention And a discharge capacity high [the irreversible capacity resulting from the side reaction in the early stages of charge is small, and] even when it is used under a big charge and discharge current is obtained. The property which was excellent in ** is shown and the lithium secondary battery which used this for the charge of lithium secondary battery negative-electrode material which solved the problem of a scale-like graphite and its manufacture approach, and a list came to be offered industrially.

[0044]

[Example] The expression approach of various physical-properties values used for the structure of the charge of lithium secondary battery negative-electrode material and a convention of a manufacturing method in this invention below and a measuring method are shown.

[0045] (1) Degree of graphitization (d_{002} , L_c)

A monochromatic X-ray is collimated to a collimated beam, the carbon powder which added the

high purity silicon as an internal standard is irradiated, and the peak corresponding to the field (002) of a graphite is measured. The spacing d_{002} between stratification planes and the magnitude L_c of C shaft orientations of microcrystal are computed by amending the peak of the silicon of an internal standard for the location and half-value width of the peak as a criterion. The concrete evaluation approach was based on what is specified in the 117th committee of Japan Society for the Promotion of Science.

[0046] (2) It measured with the BET adsorption method by specific-surface-area nitrogen gas adsorption.

[0047] (3) In the NMP (N-methyl-2-pyrrolidone) solution of electrode production and electrode performance-measurement polyvinylidene fluoride, in addition, it kneaded so that the charge powder of lithium secondary battery negative-electrode material and polyvinylidene fluoride might be set to 95 to 5 with a mass ratio, and this was applied to copper foil with a thickness of 20 micrometers, and the negative-electrode electrode foil was obtained. After drying this negative-electrode electrode foil at 80 °C and evaporating NMP, it started on 10mm square and the negative-electrode electrode was created. In order to evaluate the electrode characteristic in this negative-electrode electrode single electrode, the trilateral type cel which used the counter electrode and used the lithium metal for the reference pole was used. What dissolved LiClO_4 in the mixed solvent (they are 1:1 mixing at a volume ratio) of ethylene carbonate and diethyl carbonate at a rate of 1 mol/l was used for the electrolytic solution. About the charge and discharge test, charge and discharge were performed by the constant current consistency (0.1 mA/cm²) under potential regulation. The potential range was set to 0V to 1.5V (lithium metal criteria). While measuring first time charge capacity, first time discharge capacity, and initial charge-and-discharge effectiveness, extent of change of the discharge capacity in the charge and discharge of the 2nd henceforth estimated the cycle property.

[0048] (Example 1) After mixing 12kg in 4kg and the end of iron powder in the end of a coke breeze, it put into the graphite container, and temperature up heating was carried out in the argon air current with the Tammann electric furnace at 2000 °C, and this was cooled. After obtaining a solid reactant after a reaction, about 1kg of granular compounds which deposited in the surface section was collected. This was put into 10l. of concentrated hydrochloric acid, after holding at a room temperature for 10 hours, it filtered, and after carrying out washing filtration of this with a lot of water further, it dried at 120 °C among atmospheric air for 20 hours, and 600g of intermediate products was acquired. The jet mill ground the powder which is the acquired intermediate product, it classified with the air classifier, and 400g of powder products with a mean particle diameter of 15 micrometers was obtained. The grand total of the metal impurity by the chemical analysis of this product was 1.2 mass %. Moreover, the degrees of graphitization of this powder product are $d_{002}=0.3355\text{nm}$ and $L_c>100\text{nm}$, and had the high degree of graphitization.

[0049] To 300g of this powder graphite, coal-tar pitch (80 °C of softening temperatures) 100g was mixed, and it ****(ed) by Z mold kneader for 200 °C and 120 minutes. Gradually, viscosity was cracked after cooling the granulation object which changed into increase and a granulation condition, was put into the crucible made from a graphite, and was carbonized at the temperature of 800 °C among the lead hammer type continuous furnace. Furthermore, after putting this into the crucible made from a graphite and heat-treating and graphitizing at 3000 °C among an Atchison type graphitizing furnace, 320g of products with a mean particle diameter of 27 micrometers was obtained with a crack and air classification.

[0050] As for the degree of graphitization of the obtained product, the tap density at the time of 20

times tap was 0.73 g/cm^3 , the tap density at the time of a 300 was 1.04 g/cm^3 . $d_{002}=0.3355\text{nm}$, $L_c>100\text{nm}$, and specific surface area $1.0\text{m}^2/\text{g}$. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 0.2 mass %.

[0051] First time charge capacity is [384 mAh/g and first time discharge capacity] 368 mAh/g, and, as for the charge-and-discharge property of this ingredient, the result of 96% in initial charge-and-discharge effectiveness was obtained. Moreover, also in the charge and discharge of the 2nd henceforth, it had high electrode engine performance -- discharge capacity hardly changes but the outstanding cycle property is shown.

[0052] (Example 2) 2kg of powder was collected as steel-manufacture dust of an iron-manufacture process. This was put into 10 l. of concentrated hydrochloric acid, after holding at a room temperature for 12 hours, it filtered, and after carrying out washing filtration of this with a lot of water further, it dried at 120°C for 12 hours. The jet mill ground the obtained intermediate-product powder, it classified with the air classifier, and 800g of powder products with a mean particle diameter of 10 micrometers was obtained. The grand total of the metal impurity by the chemical analysis of this product was 2.1 mass %. Moreover, the degrees of graphitization of this powder product are $d_{002}=0.3354\text{nm}$ and $L_c>100\text{nm}$, and had the high degree of graphitization.

[0053] To 400g of this powder graphite, coal-tar pitch (80°C of softening temperatures) 120g was mixed, and it ****(ed) by Z mold kneader for 200°C and 120 minutes. Gradually, viscosity was cracked after cooling the granulation object which changed into increase and a granulation condition, was put into the crucible made from a graphite, and was carbonized at the temperature of 800°C among the lead hammer type continuous furnace. Furthermore, after putting this into the crucible made from a graphite and heat-treating and graphitizing at 3000°C among an Atchison type graphitizing furnace, 380g of products with a mean particle diameter of 25 micrometers was obtained with a crack and air classification.

[0054] As for the degree of graphitization of the obtained product, the tap density at the time of 20 times tap was 0.96 g/cm^3 , the tap density at the time of 300 tap was 1.14 g/cm^3 . $d_{002}=0.3355\text{nm}$, $L_c>100\text{nm}$, and specific surface area was $0.8\text{m}^2/\text{g}$. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 0.1 mass %.

[0055] First time charge capacity is [387 mAh/g and first time discharge capacity] 371 mAh/g, and, as for the charge-and-discharge property of this ingredient, the result of 96% in initial charge-and-discharge effectiveness was obtained. Moreover, also in the charge and discharge of the 2nd henceforth, it had high electrode engine performance -- discharge capacity hardly changes but the outstanding cycle property is shown.

[0056] (Example 3) 10kg of powder was collected as steel-manufacture dust of an iron-manufacture process. This was put into 50 l. of concentrated hydrochloric acid, after holding at a room temperature for 12 hours, it filtered, and after carrying out washing filtration of this with a lot of water further, it dried at 120°C for 12 hours. After the jet mill ground the obtained powder, air classification was performed, and 3.6kg of powder products with a mean particle diameter of 12 micrometers was obtained. The grand total of the metal impurity by the chemical analysis of this product was 2.1 mass %. Moreover, the degrees of graphitization of this powder product are $d_{002}=0.3356\text{nm}$ and $L_c>100\text{nm}$, and had the high degree of graphitization.

[0057] To 2kg of this powder graphite, coal-tar pitch (80°C of softening temperatures) 0.66kg was mixed, and it ****(ed) by Z mold kneader for 200°C and 120 minutes. Gradually, viscosity was cracked after cooling the granulation object which changed into increase and a granulation

condition, was put into the crucible made from a graphite, and was carbonized at the temperature of 1400 °C under the argon ambient atmosphere using the muffle furnace. Furthermore, it cracked, air classification of this was carried out, and 1.8kg of products with a mean particle diameter of 26 micrometers was obtained.

[0058] As for the degree of graphitization of the obtained product, the tap density at the time of a 20 times tap was 0.72 g/cm³, and the tap density at the time of a 300 times was 0.97 g/cm³. $d_{002}=0.3356\text{nm}$, $L_c>100\text{nm}$, and specific surface area was 1.2m²/g. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 0.5 mass %.

[0059] First time charge capacity is [373 mAh/g and first time discharge capacity] 354 mAh/g, and, as for the charge-and-discharge property of this ingredient, the result of 95% in initial charge-and-discharge effectiveness was obtained. Moreover, also in the charge and discharge of the 2nd henceforth, it had high electrode engine performance -- discharge capacity hardly changes but the outstanding cycle property is shown.

[0060] (Example 4) After mixing 3kg and 12kg of nickel powder in the end of a coke breeze, it put into the graphite container, and temperature up heating was carried out among the argon air current with the Tammann electric furnace at 2200 °C, and this was cooled. After obtaining a solid reactant after a reaction, about 750g of granular compounds which deposited in the surface section was collected. This was put into 1l. of 1:1 mixed solutions of concentrated nitric acid and fluoric acid, after holding at a room temperature for 12 hours, it filtered, and further, after carrying out washing filtration of this with a lot of water, it dried at 120 °C for 12 hours. After the jet mill ground the obtained powder, sieve classification was carried out and 370g of powder products with a mean particle diameter of 12 micrometers was obtained. The grand total of the metal impurity by the chemical analysis of this product was 1.9 mass %. Moreover, the degrees of graphitization of this powder product are $d_{002}=0.3355\text{nm}$ and $L_c>100\text{nm}$, and had the high degree of graphitization.

[0061] To 300g of this powder graphite, coal-tar pitch (80 °C of softening temperatures) 150g was mixed, and it ****(ed) by Z mold kneader for 200 °C and 120 minutes. Gradually, viscosity was cracked after cooling the granulation object which changed into increase and a granulation condition, was put into the crucible made from a graphite, and was carbonized at the temperature of 800 °C among the lead hammer type continuous furnace. Furthermore, after putting this into the crucible made from a graphite and heat-treating and graphitizing at 3000 °C among an Atchison type graphitizing furnace, 290g of products with a mean particle diameter of 25 micrometers was obtained with a crack and air classification.

[0062] As for the degree of graphitization of the obtained product, the tap density at the time of 20 times tap was 0.74 g/cm³ and the tap density at the time of a 300 tap was 0.97 g/cm³. and $d_{002}=0.3355\text{nm}$, $L_c>100\text{nm}$, and specific surface area was 1.1m²/g. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 0.6 mass %.

[0063] First time charge capacity is [386 mAh/g and first time discharge capacity] 370 mAh/g, and, as for the charge-and-discharge property of this ingredient, the result of 96% in initial charge-and-discharge effectiveness was obtained. Moreover, also in the charge and discharge of the 2nd henceforth, it had high electrode engine performance -- discharge capacity hardly changes but the outstanding cycle property is shown.

[0064] (Example 5) After mixing 1kg and 8kg of silicon powder in the end of a coke breeze, it put into the graphite container, and temperature up heating was carried out in the argon air current with the Tammann electric furnace at 2500 °C, and this was cooled. After obtaining a solid

reactant after a reaction, about 600g of granular compounds which deposited in the surface section was collected. This was put into 1l. of 1:1 mixed solutions of concentrated nitric acid and fluoric acid, after holding at a room temperature for 12 hours, it filtered, and further, after carrying out washing filtration of this with a lot of water, it dried at 120 °C for 12 hours. After the ball mill ground the obtained powder, sieve classification was carried out and 350g of powder products with a mean particle diameter of 15 micrometers was obtained. The grand total of the metal impurity by the chemical analysis of this product was 7.5 mass %.

[0065] To 300g of this powder graphite, coal-tar pitch (80 °C of softening temperatures) 90g was mixed, and it ****(ed) by Z mold kneader for 200 °C and 120 minutes. Gradually, viscosity was cracked after cooling the granulation object which changed into increase and a granulation condition, was put into the crucible made from a graphite, and was carbonized at the temperature of 800 °C among the lead hammer type continuous furnace. Furthermore, after putting this into the crucible made from a graphite and heat-treating and graphitizing at 3000 °C among an Atchison type graphitizing furnace, 370g of products with a mean particle diameter of 22 micrometers was obtained with a crack and air classification.

[0066] As for the degree of graphitization of the obtained product, the tap density at the time of and a 20 times tap was 0.96 g/cm³ and the tap density at the time of 300 was 1.14 g/cm³. $d_{002}=0.3355\text{nm}$, $L_c>100\text{nm}$, and specific surface area was 1.0m²/g. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 0.1 mass %.

[0067] First time charge capacity is [380 mAh/g and first time discharge capacity] 361 mAh/g, and, as for the charge-and-discharge property of this ingredient, the result of 95% in initial charge-and-discharge effectiveness was obtained. Moreover, also in the charge and discharge of the 2nd henceforth, it had high electrode engine performance -- discharge capacity hardly changes but the outstanding cycle property is shown.

[0068] (Example 6) After mixing 2kg and 8kg of cobalt powder in the end of a coke breeze, it put into the graphite container, and temperature up heating was carried out in the argon air current with the Tammann electric furnace at 2200 °C, and this was cooled. After obtaining a solid reactant after a reaction, about 400g of granular compounds which deposited in the surface section was collected. This was put into 1l. of 1:1 mixed solutions of concentrated nitric acid and fluoric acid, after holding at a room temperature for 12 hours, it filtered, and after carrying out washing filtration of this with a lot of water further, 120 °C dried for 12 hours. After the jet mill ground the obtained powder, sieve classification was carried out and 5g of powder products with a mean particle diameter of 38 micrometers was obtained. The grand total of the metal impurity by the chemical analysis of this product was 1.5 mass %.

[0069] Thus, to prepared carbon material 200g, coal-tar pitch (80 °C of softening temperatures) 67g was mixed, below, by the same technique as an example 1, carbonization, graphitization, the crack, and the classification were performed and 220g of products with a mean particle diameter of 25 micrometers was obtained.

[0070] As for the degree of graphitization of the obtained product, the tap density at the time of and a 20 times tap was 0.73 g/cm³ and the tap density at the time of 300 was 0.98 g/cm³. $d_{002}=0.3355\text{nm}$, $L_c>100\text{nm}$, and specific surface area was 1.0m²/g. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 0.1 mass %.

[0071] First time charge capacity is [376 mAh/g and first time discharge capacity] 360 mAh/g, and, as for the charge-and-discharge property of this ingredient, the result of 96% in initial charge-and-discharge effectiveness was obtained. Moreover, also in the charge and discharge of

the 2nd henceforth, it had high electrode engine performance -- discharge capacity hardly changes but the outstanding cycle property is shown.

[0072] (Example 1 of a comparison) After the ball mill ground the natural graphite, sieve classification was carried out, and powder with a mean particle diameter of 15 micrometers was obtained. The grand total of the metal impurity of this graphite is 0.4 mass %, and had the degree of graphitization with a as high degree of graphitization as $d_{002}=0.3355\text{nm}$ and $L_c>100\text{nm}$. To 300g of this natural graphite powder, 50g was mixed and the coal-tar pitch (80 °C of softening temperatures) was ****(ed) by Z mold kneader for 200 °C and 120 minutes. Gradually, viscosity was cracked after cooling the granulation object which changed into increase and a granulation condition, was put into the crucible made from a graphite, and was carbonized at the temperature of 800 °C among the lead hammer type continuous furnace. Grain-size preparation of this was carried out at 25 micrometers of mean diameters, and it put into the crucible made from a graphite, and heat-treated and graphitized at 3000°C among the Atchison type graphitizing furnace.

[0073] As for the degree of graphitization of the obtained product, the tap density at the time of and a 20 times tap was 0.77 g/cm^3 and the tap density at the time of 300 was 0.68 g/cm^3 . $d_{002}=0.3355\text{nm}$, $L_c>100\text{nm}$, and specific surface area was $1.7\text{m}^2/\text{g}$. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 0.1 mass %.

[0074] First time charge capacity was [390 mAh/g and the first time discharge capacity of the charge-and-discharge property of this ingredient] 345 mAh/g, and initial charge-and-discharge effectiveness was the result of calling it 88%.

[0075] (Example 2 of a comparison) Steel-manufacture dust 2kg of the same iron-manufacture process as an example 2 was collected. By the same approach as an example 2, concentrated hydrochloric acid washing, backwashing by water, desiccation, grinding, and a classification were performed for this, and 800g of powder products with a mean particle diameter of 10 micrometers was obtained. The grand total of the metal impurity by the chemical analysis of this product was 2.2 mass %. Moreover, the degrees of graphitization of this powder product are $d_{002}=0.3356\text{nm}$ and $L_c>100\text{nm}$, and had the high degree of graphitization.

[0076] To 400g of this powder graphite, coal-tar pitch (80 °C of softening temperatures) 120g was mixed, and it ****(ed) by Z mold kneader for 200 °C and 120 minutes. Viscosity was cracked gradually after cooling the granulation object which changed into increase and a granulation condition, and it put into the crucible made from a graphite, and heat-treated at the temperature of 600 °C among nitrogen-gas-atmosphere mind with the experimental reactor. Furthermore, 480g of products with a mean particle diameter of 25 micrometers was obtained for this with a crack and air classification.

[0077] As for the degree of graphitization of the obtained product, the tap density at the time of and 20 times tap was 0.56 g/cm^3 and the tap density at the time of 300 was 0.70 g/cm^3 . $d_{002}=0.3360\text{nm}$, $L_c>100\text{nm}$, and specific surface area was $11\text{m}^2/\text{g}$. Moreover, the grand total of the metal impurity by the chemical analysis of the obtained product was 2.1 mass %.

[0078] First time charge capacity is [349 mAh/g and first time discharge capacity] 297 mAh/g, and, as for the charge-and-discharge property of this ingredient, the result of 85% in initial charge-and-discharge effectiveness was obtained. Moreover, in the charge and discharge of the 2nd henceforth, discharge capacity decreased gradually and about 20% of degradation was accepted after the charge and discharge which are 30 times compared with the 1st discharge capacity.

[0079] The engine performance of the graphite material obtained in the examples 1 and 2 of a comparison is known by that the electrode characteristic of discharge capacity, initial charge-and-discharge effectiveness, and a cycle property is excellent in the direction of the graphite material of this invention as compared with examples 1-6.

[0080]

[Effect of the Invention] While having a discharge capacity comparable as a discharge capacity of scale-like graphites, such as a natural graphite, of the highest level, or the geometric capacity determined from graphite structure as a carbon material for lithium secondary battery negative electrodes by this invention And the irreversible capacity resulting from the side reaction in the early stages of charge was large, and when it was used under a big charge and discharge current, the charge of lithium secondary battery negative-electrode material which solved the problem of a scale-like graphite -- a high discharge capacity is not obtained -- and its manufacture approach were offered. Moreover, it became usable [further small and lightweight-izing of a pocket device etc., or long duration] by high capacity with the lithium secondary battery of this invention using a negative-electrode ingredient with high charge-and-discharge effectiveness.

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